HEAVY METAL CONCENTRATIONS IN TISSUES OF COMMERCIALLY EXPLOITED FISH (*Oreochromis niloticus baringoensis, Protopterus aethiopicus, Clarias gariepinus)* FROM LAKE BARINGO, KENYA

MBUTHIA JUDY WANJIRU

Thesis Submitted to the Graduate School in Partial Fulfillment of the Requirements for the award of Master of Science Degree of Environmental and Occupational Health of Egerton University

EGERTON UNIVERSITY

OCTOBER, 2015

DECLARATION AND RECOMMENDATION

DECLARATION

This thesis is my original work and has not been submitted or presented for examination in any other institution either in part or as a whole.

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

Mbuthia Judy Wanjiru
NM15/3359/12

RECCOMMENDATION

This thesis has been submitted for examination with our approval as university supervisors.

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

Dr. George Morara Ogendi
Department of Environmental Science
Egerton University

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

Dr. Wilkister Nyaora Moturi
Department of Environmental Science
Egerton University

COPYRIGHT

DEDICATION

This work is dedicated to my husband Isaac Muchiri and to my parents Mr and Mrs Josphat Mbuthia.

ACKNOWLEDGEMENTS

I thank the Almighty God for granting me good health and strength throughout my study period.

I would like to express my sincere appreciation to my academic supervisors Dr. George Morara Ogendi and Dr. Wilkister Nyaora Moturi for their inspiring guidance, assistance, supervision, encouragement, tolerance, devotion and support to all my endeavors during the study and in the preparation of this thesis. I pass my gratitude to Egerton University Division of Research and Extension for providing me with the much needed funds to carry out the research. The research was through an internally funded research project with Dr. Ogendi as the principal investigator.

My special thanks to fishermen and fishmongers at the shores of Lake Baringo, led by Madam Phoebe. Thank you for the invaluable help, expertise, cordiality and hospitality as well as the willingness to give information throughout the research period. I would also like to register my gratitude to NAWASSCO team for their invaluable assistance with my laboratory work.

I thank my family for the encouragements and untiring moral and financial support. I pass my appreciation to my loving husband Isaac, for putting up with my schedules and supporting my endeavors.

Last but not least I would like to thank the entire Egerton fraternity, lecturers and course mates and all persons who contributed in any way in making my research and thesis writing a success.

ABSTRACT

Studies have shown that elevated heavy metal concentrations in water and sediments may be biomagnified along the aquatic food chains/webs and eventually affecting human health through the consumption of metal-contaminated water and/or fish from such water bodies. This study was conducted to assess the concentration of heavy metals in the tissues of *Oreochromis niloticus baringoensis*, *Protopterus aethiopicus* and *Clarias gariepinus* fish species of Lake Baringo and compare the results with WHO guideline values. Water and fish samples were collected from five selected sites in six sampling occasions and the analyses for heavy metals (i.e. Cu, Hg, Cd, Pb) in fish and water samples was done using the Atomic Absorption Spectrophotometer at Nakuru Water and Sewerage Company Laboratory. There was a significant difference in physical chemical parameters from all sites in Lake Baringo except for temperature. Copper, Cadmium and mercury were available in measurable quantities in water samples but lead was below detection limit (<0.026). There was no significant difference in heavy metal concentration in all the tilapia (F=0.88, P=0.44), lungfish (F=0.99, P=0.43) and catfish (F=0.09, P=0.70) samples collected from different sampling sites. The pooled heavy metal concentration levels recorded in fish for Copper, Cadmium and Zinc was 0.473±0.125, 3.565±0.063 and 24.398±3.262 respectively. Therefore the heavy metal concentration in fish decreased in the sequence Zinc>Cadmium>copper. Lead and Mercury concentrations in fish samples were below the limits of instrument detection. Copper, Lead and Mercury concentration in fish were below WHO guideline values thus posing more of an environmental than human health concern. However, Cadmium and Zinc concentration was above WHO guideline values thus posing a human health concern. Regular monitoring of the Lake Baringo water quality is therefore necessary to record any variation in the water quality and heavy metal concentration in fish in order to curb heavy-metal related health effects arising from consumption of heavy metal contaminated fish.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS AND ACRONYMS

Cd- Cadmium

Cu- Copper

Fe-Iron

Hg-Mercury

Pb-Lead

Zn-Zinc

PUFAs- Polyunsaturated Fatty Acids

WHO- World Health Organisation

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background Information

Heavy metals in the aquatic ecosystems are of global concern due to their bioaccumulation, biomagnification ability and toxicity in low concentration thus posing potential negative impacts to the environment and human health. Heavy metals are released to the environment from anthropogenic activities such as metal production, agricultural activities, mining and industrial development. These metals are also as a result of natural geochemical processes such as volcanic eruptions and forest fires. The continued increase in human population has amplified the release of heavy metals in lakes (Storelli, 2008).

Heavy metals have wide environmental dispersion (Ishaq, 2011), with the tendency to accumulate in selective tissues (Bezuidehout *et al*,1990), of the living organisms and have overall potential to be toxic even at relatively low levels of exposure (Hu, 2002). In the aquatic ecosystem, heavy metals may bioaccumulate in various organs of aquatic organisms, especially fish, which in turn may enter the human metabolism through consumption causing serious health hazards (Shrivastava, 2011). Heavy metals enter the fish through gills, skin, oral in food and water. In the fish body, the metal is transported through the blood stream and either stored, transformed or eliminated in the liver, kidney or the gills (Ishaq, 2011)

Fish consumption can be an important route of human exposure to a variety of heavy metals such as mercury, lead, cadmium and copper as fish is often at the top of aquatic food chain and may, therefore, concentrate large amounts of some heavy metals from the water (Storelli, 2008). Globally, fish is preferred as an important source of proteins, minerals, vitamins and polyunsaturated fatty acids (PUFAs), especially omega-3 PUFAs. Fish consumption reduces the risk of coronary heart disease, decreased mild hypertension and prevents certain cardiac arrhythmias (Mozaffarian , 2006).

Human health effects from heavy metal contaminated fish are an issue of global concern. Such a case has been documented in Japan where major factories discharged their waste into water bodies resulting into contamination of fish thereby causing adverse effects on human health. This led to the outbreak of the Minamata disease in 1956 around Minamata Bay, in Kumamoto prefecture (Museum, 2007). Minamata disease was as a result of consumption of methylmercury-contaminated seafood. This disease affects the central nervous system resulting into ataxia, hearing impairment, narrow vision and speech impediments. Cases of congenital Minamata were also recorded as a result of methylmercury poisoning of the fetus via the placenta due to consumption of contaminated seafood by the mother (Kurland *et al*, 2001).

The increase in industrial activities and urbanization in Africa has lead to a massive increase of heavy metals in the natural environment. Anthropogenic activities releasing heavy metals include leather tanning, electroplating, and combustion of leaded petrol, intensive agriculture and sludge dumping (Alo, 2006). Heavy metals have been recorded in Ogu River, Nigeria (Farkas & Adelowo, 2007), Lake Kariba, Zimbabwe (Berg *et al*, 1995) and Nasser Lake (Rasheed, 2008).

Kenyan aquatic ecosystems have been reported to have high concentration of heavy metals, both in fish and water (Campbell *et al*, 2003; Mwashote, 2003;Muiruri *et al*, 2013). Lake Baringo is a fresh water lake in the Rift Valley that supports a variety of fish populations, providing subsistence food to the local communities, as well as, a source of income. The fish community of Lake Baringo comprises of seven species with the endemic Baringo Tilapia (*Oreochromis niloticus baringoensis)* being the predominant species that contribute greatest to the commercial fishery and highly regarded for their nutritional value. The other fish species, in the order of their commercial importance, include Lungfish *(Protopterus aethiopicus),* African sharptooth Catfish *(Clarias gariepinus*), barbus *(Barbus gregorii),* Redeye Labeo *(Labeo cylindricus),* Line-spotted barb *(Barbus lineomaculatus)* and *Aplocheilichthys* species (Hickley *et al*., 2004).

The Lake Baringo water catchment areas have been intensely degraded through deforestation and conversion into agricultural farms (Hickley *et al*., 2004). Owing to the numerous anthropogenic activities on the catchment areas, the water quality of the feeder rivers may be impaired due to high concentrations of dissolved organic and inorganic substances such as heavy metals and potassium, magnesium, sulphate and chlorine (Odada, 2005). Apart from the inflowing rivers, other possible sources of heavy metals in Lake Baringo include tourism activities particularly the use of boats to ferry tourists to various destination points on the lake and rapid urbanization of the surrounding areas of the lake. The study, therefore, specifically identified the potentially toxic heavy metals in Lake Baringo, quantified their concentrations in water and commercially exploited fish species at various points on the lake and determined whether these heavy metal levels in selected fish species are within WHO guideline values.

1.2 Statement of the Problem

The rapid increase in human population around Lake Baringo drainage basin, growing at a rate of 2.65% per annum, has increased the demand for fish from Lake Baringo. The exploited fish species given their position in the aquatic food chain have the potential of accumulating substantial amounts of heavy metals in the soft and hard tissues thus posing health risks to fish consumers. Most of the fish for subsistence consumption hardly go through health inspectors and, therefore, a high likelihood that a greater portion of the population within the Lake will be affected if they consume metal-contaminated fish. Heavy metals are of particular concern because of their environmental persistence, toxicity at low concentration and the ability to bioaccumulate along the food chain. Heavy metals are also potent neurotoxicants and can adversely affect the developing brain of fetus, infants, and young children. Heavy metals can also lead to cardiovascular, reproductive and renal effects in chronic exposures. The study therefore, assessed concentrations of mercury, lead, Zinc, cadmium and copper, specifically, in tissues of commercially exploited fish and compared the study values with WHO guideline values.

1.3 Objectives

1.3.1 Broad objective

To contribute to the understanding of the level of heavy metal concentrations in tissues of commercially exploited fish species (*Oreochromis niloticus baringoensis, Protopterus aethiopicus, Clarias gariepinus)* of Lake Baringo, Kenya.

1.3.2 Specific objectives

1. To characterize the physical chemical parameters (pH, temperature, conductivity, dissolved solids and salinity) of water Lake Baringo.
2. To determine the concentrations of selected heavy metals (Copper, Mercury, Cadmium, Zinc and Lead) in water samples taken from different sampling points in Lake Baringo.
3. To determine the concentrations of the selected heavy metals (Copper, Mercury, Cadmium, Zinc and Lead) in tissues of selected fish species (*Oreochromis niloticus baringoensis, Protopterus aethiopicus, Clarias gariepinus)* of Lake Baringo.

1.4 Research questions

1) Is there is any variation in physical chemical parameters in Lake Baringo?
2) Is there significant difference in concentrations of selected heavy metals in water samples collected from different sites in Lake Baringo?
3) Is there variation in concentrations of selected heavy metals in tissues of the selected fish species obtained from Lake Baringo?

1.5 Justification

Lake Baringo is a Ramsar site in Kenya that is under threat of heavy metal pollution from agricultural activities, waste from surrounding urban centres and human settlements within the lake's catchment area. Tourism activities such as the use of motor boats lead to oil pollution which partly contributes to the heavy metal contaminants into the lake. Increased human population around Lake Baringo has resulted to an increase in demand for fish as a source of food. The major commercially exploited fish in Lake Baringo include, *Oreochromis niloticus baringoensis, Protopterus aethiopicus* and *Clarias gariepinus,* which form an important staple food as a source of proteins, minerals, vitamins and polyunsaturated fatty acids to the local community. These fish species may form an important route of human exposure to a variety of heavy metals such as mercury, lead, cadmium and copper as fish is often at the top of aquatic food chain and may, therefore, concentrate large amounts of some heavy metals from the water.

Consumption of heavy metal- contaminated fish can lead to various health risks such as cancer, neurological, cardiovascular, renal and gastrointestinal complications. Human health is therefore more likely to be negatively affected through consumption of metal-contaminated fish which justifies this study. Determining heavy metal concentration in the fish tissues will serve an important function as an early warning indicator of heavy metal contamination of Lake Baringo ecosystem. The study findings are important for continuous monitoring of contaminants in Lake Baringo and form a baseline for further assessment of human health risks from heavy metal poisoning.

1.6 Scope of the Study

The study was part of an extensive research in Lake Baringo, "An assessment of heavy metal concentrations in water, sediments and fish tissues of commercially exploited fish species in Lake Baringo, Kenya". The study was limited to the major commercially exploited fish species of Lake Baringo, that is, *Oreochromis niloticus baringoensis, Protopterus aethiopicus* and

Clarias gariepinus. The samples were collected from 5 sampling sites (S1-Kampi ya Samaki discharge point; S2-Endau River discharge point; S3-Salabani discharge point; S4-Molo River discharge point, and; S5-Ol- Kokwar). A total of 40 samples (2 replicates X 5 sites X 4 sampling occasions), for both water and fish, were collected by the end of the study. The physical-chemical parameters, that is, (temperature, conductivity, and dissolved oxygen) were measured insitu. Heavy metal concentration in fish tissues and water was determined. The fish heavy metal concentration was compared with the WHO guideline values to determine the safety of the fish for human consumption.

1.7 Definition of Terms

Acquired ataxia- refers to a collection of disorders, including the loss of balance and physical coordination leading to difficulty walking, speaking and poor vision due to damaged cerebellum or other parts of nervous systems. These disorders are as a result of nutritional intake of heavy metal-contaminated food (WHO, 2010).

Bioaccumulation- the process by which the heavy metal concentration in fish attains a point that surpass that in water as a consequence of heavy metal uptake via every probable way of chemical contact, for instance, nutritional assimilation, movement across the respiratory surface, absorption through the skin and inhalation (Jezierska, 2006).

Bioconcentration- the process whereby heavy metal concentration in an aquatic fish surpass that in water as an outcome of contact with waterborne chemical assimilation from the water through the respiratory surface, for instance, gills and the skin (Jezierska, 2006).

Biomagnification- this is a scenario whereby, heavy metal concentration increases along a food chain as a result of persistence (not easily broken down by environmental processes) or low rate of internal degradation (Babatunde *et al*, 2012).

Heavy metal- a metallic substance with high atomic weight such as mercury, chromium, cadmium and lead that can damage living things at low concentration and tend to accumulate in the food chain (USEPA, 2000).

Methylation- this is the addition of a methyl group to a substrate or the substitution of an atom or group by a methyl group and leads to modification of heavy metals (Farkas & Adelowo, 2007).

Necrosis- this is a disorder due to heavy metal toxicity that involves the death of body tissues that is not reversible and occurs when there is no enough blood flowing to the tissues (Hu, 2002).

Osteomalacia- this is a muscle-skeletal disorder whereby the bones become very soft and more likely to bow and fracture and results from defect in the bone-building process especially due to heavy metal toxicity(WHO, 2010).

Osteoporosis- this is a skeletal problem whereby the bones become fragile and more likely to fracture. Bones become less dense by loss of density which is a measure of calcium and minerals in the bone (Storelli, 2008).

Polyunsaturated fatty acids (PUFAS) - these are unsaturated fatty acid whose carbon chain has more than one double or triple valence bond per molecule. They are mainly found in fish (Storelli, 2008).

Toxicity-this refers to the quality or relative degree of a heavy metal being toxic or poisonous to living things. Heavy metal toxicity can result in considerable human mortality and morbidity (Mozaffarian, 2006)

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

Heavy metals have been variously defined using specific gravity and the atomic weight. According to Merrian, heavy metals are metals with a specific gravity of 5.0 or greater (Merriam, 1976). Holister and Porteous (1976) defines the heavy metal as a metal with high atomic weight greater than 40. The study adopted the definition according to United States Environmental Protection Agency that a heavy metal is a metallic substance with high atomic weight such as mercury, chromium, cadmium and lead that can damage living things at low concentration and tend to accumulate in the food chain (EPA, 2000).

According to various studies done on lakes and rivers, heavy metals have become common pollutants that have detrimental effects on these ecosystem health as well as potential adverse human health effects (Kurland *et al*, 2001; Campbell *et al*, 2003; Mwashote, 2003; Alo, 2006; Farkas and Adelowo, 2007; Safahieh, 2011; Muiruri *et al*, 2013;). Heavy metal pollution comes from point source and non-point sources (Zheng & Li, 2007; Shinn, 2009;Ishaq, 2011; Vijayakumar, 2011). The largest source of heavy metals in water is the natural geological weathering of soil and rocks that directly expose these metals to surface water. Through anthropogenic activities such as agricultural activities, mining and industrial manufacturing, heavy metals have gradually increased in the natural aquatic ecosystems.

Anthropogenic activities increase the concentration of heavy metals in water bodies. These activities include agriculture and deforestation. Agricultural activities involve the use of various agrochemicals (such as pesticides and herbicides) and fertilizers which contain various heavy metals. Through agricultural run-off, these heavy metals end up in water bodies. Forests are known as buffers to soil erosion reduce the velocity and help in uptake of substances in surface runoff, therefore, reducing the amount reaching into lakes. Deforestation will, therefore, increase heavy metal concentration in lakes (Jezierska, 2006). Environmental pollution especially by plastics, metals, oils, pharmaceutical equipments, batteries and mineral tailings add a lot of heavy metals in the natural environment which end up into water bodies via surface run-off. Waste disposal methods such as use of incinerators also contribute to high levels of non point heavy metal pollution (Shrivastava, 2011).

Heavy metals are of particular concern because of their environmental persistence, toxicity at low concentration and the ability for bioconcentration, bioaccumulation and biomagnification (Vijayakumar, 2011). Fish are in close and constant contact with water and therefore contamination of water by heavy metals will definitely end up in fish through uptake via various media (Schmitt *et al*, 2005). Fish gills are contaminated through the process of gaseous exchange, especially the uptake of oxygen from water passing over the gills (Ishaq, 2011).

Uptake of heavy metals by fish occurs through various routes which are; food, non-food particles, through the gills and skin. The importance of these uptake routes vary greatly depending on the bioavailability of the heavy metal in question. Aquatic organisms can take up heavy metals through their digestive systems and hence elevating the possibility of metal entry into the human food chain (Obasohan, 2007). Metal uptake through food is quite substantial. This is due to heavy metal uptake by plants that is an important route that making heavy metals present in the sediments bioavailable for the herbivorous fish (Berg *et al*, 1995).

Heavy metals are commonly found in trace concentrations in, natural waters and some are essential to living organisms, yet they may become highly toxic when present in high concentrations (Hu, 2002). Some heavy metals such as cobalt, copper, iron manganese, molybdenum, vanadium, strontium and zinc are essential for the growth and survival of living organisms. However, excessive levels of essential metals can pose a health risk to humans and can have environmental effects on aquatic organisms. Non-essential heavy metals of particular concern to surface water systems are cadmium, chromium, mercury, lead and arsenic (Ishaq, 2011).

Essential metals are important for growth and development, and their uptake from the environment is regulated according to nutritional demand through homeostatic control. Heavy metals are non-essential metals that do not have dedicated regulatory mechanisms in the body and are, therefore, more toxic to human beings (Shinn *et al*, 2009). Non-essential heavy metals of particular concern to aquatic ecosystems are cadmium, chromium, mercury, lead and arsenic (Ishaq, 2011).

In aquatic ecosystems, only few metals such as cadmium, copper, lead and zinc are occur as dissolved ions. However, most metals are present as complexes, colloids and suspended ions. Heavy metal concentration in fish is dependent on age, body size. Heavy metal bioaccumulation in fish is dependent on physiological factors (absorption rate, accumulation and growth), chemical factors (bioavailability, metal speciation and concentration), and environmental factors such as temperature and pH.

Heavy metals have the tendency of biomagnifying and bioaccumulate in various organs of aquatic organisms, especially fish, which is often at the top of aquatic food chain in an aquatic ecosystem (Shrivastava, 2011). Therefore, fish consumption can be an important route of human exposure to a variety of heavy metals such as mercury, lead, cadmium and serious health hazards (Storelli, 2008). Studies indicate significant seasonal differences in concentration of heavy metals in fish tissues. Chouba *et al* (2007) found that lead concentration was high during winter than during summer. Concentration of heavy metals also varies among various fish organs. Concentration of heavy metals in any organ depends on its rate of absorption and the dynamic process associated with its elimination by the fish (Bezuidehout *et al*, 1990; Mwashote, 2003; Nemr, 2003; Schmitt *et al*, 2005). Giordano *et al* (1991) concluded that various fish species concentrate mercury differently. In his study in the Italian Coastal water, he found out that *serranus scriba* had high mercury concentration than *serranus cabrilla*.

Heavy metals are known to be denser than water by approximately five times and therefore more stable and easily bioaccumulate in fish tissues. Heavy metal concentration in fish is directly proportional to the concentration of heavy metal concentration in the surrounding environment especially through waterborne uptaa) (Babatunde, Oyebanjo, & Adeolu, 2012). Heavy metals in aquatic environment are present in labile and non-labile soluble forms and in particulate forms. The labile forms of metal ions are the most dangerous as they are more bioavailable and easily taken up by fish (Anim *et al*. 2011).

Fish feeding behavior affects heavy metal accumulation in fish tissues. Predatory fish feeding on small fish and zooplanktons accumulate more metals than non-predatory fish and benthivores feeding mostly on phytoplanktons. A fish that is a specific feeder will concentrate high levels of heavy metals than a fish that has a generalized feeding habit (Griesbauer, 2007).

2.2 Characteristics and Ecology of the Selected Fish Species

Aquatic organisms especially fish species are extensively used in biomonitoring studies in order to know the variation in environmental levels of anthropogenic pollutants. Fish given their position in the aquatic food web can be used to indicate the pollution status of the ecosystem as they are sensitive to many pollutants. Fish have a very intimate contact with water that could be carrying heavy metals in suspension and solution as they have to extract oxygen using the gills. Tilapia *(Oreochromis niloticus baringoensis)*, Marbled Lungfish (*Protopterus aethiopicus*) and Catfish *(Clarias gariepinus)* fish species were selected for the study because they constitute the dominant species in the commercial fishery at Lake Baringo. These fish are also highly regarded for their high nutritional value (Odada, 2005).

Tilapia *(Oreochromis niloticus baringoensis)* also known as *Ngege* to the locals, is a subspecies of Nile Tilapia (*Oreochromis niloticus niloticus*. The fish is endemic to Lake Baringo and forms the most important commercial fish (Britton *et al*, 2008). The body colour of the males is red-pink with many silver scales and a black throat while the females are brown with some red throat. The fish can reach up to ten inches with females being 7-8 inches (Borstein, 2006). Tilapia can live in very low oxygenated waters, in many pH ranges and in the temperature range from 40 to 110 Fahrenheit. Tilapia mainly feeds on algae, diatoms, rotifers, mollusks and copepods (Kariman *et al*, 2009).

Marbled Lungfish (*Protopterus aethiopicus*) otherwise known as *Kamongo* by the lake Baringo local community, is snake-like fish that inhabits shallow water, inshore waters including the dense interior of swamps and marshes. The principal diet consists of mollusks, small fish and insects. It is highly preferred as a food fish by the fishermen and the consumers because of its strong taste of flesh (Kees & Frans, 2002).

Catfish *(Clarias gariepinus)*, also known as Mumi by the local community, occurs in a wide variety of freshwater habitats and feeds on phytoplanktons and benthic algae. It is a benthopelagic dioecious fish tolerant to extreme environmental conditions and can survive temperatures between 14°C and 33°C. This fish is highly commercial as food fish and is marketed fresh and frozen (FAO, 2010).

2.3 Selected Heavy Metals, Sources, Physical Characteristics and Their Impacts on Human Health

Cadmium is a soft bluish-white metallic element that is produced as a by-product of zinc, copper and lead mining and smelting. This metal is widely used in electroplating and production of steel and polyvinyl chloride (PVC), nickel-cadmium batteries, fertilizers, pigments, ceramics and textiles. Human activities such as incineration of municipal waste containing batteries and plastics, land application of sewage sludge and phosphate fertilizers, as well as, disposal of electronic waste has led to an increase in the availability of cadmium in the environment (WHO, 2010).

For nonsmokers, food is generally the largest source of exposure to cadmium poisoning. The population at highest risk consists of women with nutritional deficiencies, people with kidney disorders, and fetuses and children with low body iron stores (Hu, 2002). The kidney is the critical Cadmium target organ in the body which leads to renal tubular dysfunction. High Cadmium concentration in the body can cause skeletal effects such as osteoporosis and osteomalacia. Other effects include hepatic necrosis, renal necrosis, hemorrhagic gastroenteritis and high risk of cancer (lungs, kidney, prostate and stomach) (Evangelou, 1998). Maternal exposure to cadmium is associated with low birth weight and an increase of spontaneous abortion (Flavo, 2008).

Mercury present in the atmosphere is released from industrial activities such as battery production, mining, smelting and fossil fuel combustion and is deposited onto soil and waterways. The most poisonous form of mercury in aquatic ecosystems is Methylmercury which is a result of mercury methylation by microorganisms. Methylmercury readily accumulates in fish tissues through bioaccumulation and, therefore, becomes exposed to fish consumers. Methylmercury readily crosses the placenta and enters the fetal brain, where it impairs normal development (NJDEP, 2012). Prenatal exposure to even low levels of mercury may result in neurological damage causing deficiencies in motor skills, attention, language skills, learning capacity, and memory in children. Mercury also passes through breast milk, which is an additional reason to minimize mercury exposure among breastfeeding mothers (Griesbauer, 2007).

Lead is present in storage batteries, gasoline additives, pigments, ammunition, varnishes, plastics, metal alloys, effluents from industry and mining, coal combustion and gasoline exhaust. Lead affects multiple body systems resulting into acute and chronic effects on human health, which include neurological, cardiovascular, renal, gastrointestinal, hematological, and reproductive effects (WHO, 2010). Lead is one of the most dangerous chemicals for children and developing fetuses. Other vulnerable population groups include socially and economically disadvantaged populations and the malnourished, whose diets are deficient in proteins and calcium (Flavo, 2008).

Copper is widely used in the electrical industry for wire, water pipes, cooking utensils, roofing materials, pigments and chemical and pharmaceutical equipments. Copper sources in the aquatic environment include mining, metal plating and industrial effluents. Copper is required for normal metabolic processes as an essential micronutrient (Santos, 2010). However at high doses, copper causes vomiting, diarrhea, nausea and headache while chronic copper toxicity results into gastrointestinal bleeding, haematuria, intravascular haemolysis and acute renal failure (WHO, 2010).

2.5 Nutritional and Economic Benefits of Fish Consumption

According to FAO (2012), approximately five billion people depend on fish for more than 20% dietary animal protein. Fish form the most extracted wildlife in the world with over 140 million tonnes annually. The freshwater fisheries in developing countries form approximately 94% of all freshwater fisheries in the world. Fish and fisheries activities provide a livelihood and food for most of the world's poorest people. Fish contributes to the economic wellbeing of many people in developing countries through nutrition, export, recreation and tourism (FAO, 2012).

Fish is regarded as an important part of a healthy diet and a boost to food security because of its nutritional benefits. Ensuring that people at all times have social, physical and economic access to nutritious and safe food to meet their daily nutritional needs is regarded as food security (Belton, 2011). In this context, fish is important as it forms an affordable and in most cases, the only source of animal protein for most people in developing countries (FAO, 2010).

Fish constitutes an important source of proteins, minerals, vitamins and polyunsaturated fatty acids (PUFAs); especially omega-3 fatty acids required for good growth of the nervous system and the brain in the fetus and children and can reduce the danger of suffering a heart attack. Fish consumption reduces the risk of coronary heart disease, decreased mild hypertension and prevents certain cardiac arrhythmias (Mozaffarian & Eric, 2006). Fish are thus an exceptional alternative for other protein foodstuffs that have elevated levels of saturated fats and cholesterol. Fish also contains niacin and vitamin B6 and vitamin D. Eating fish can contribute to a healthy heart and a child's proper growth and intellectual development (Belton, 2011).

As many small fishes are eaten whole, with head, organs and bones, they are a particularly good source of calcium, and some are also rich in vitamin A, iron and zinc. Vitamin A is present as dehydroretinol and retinol found mainly in the eyes and viscera. Iron is present in the forms of haem-iron, a high molecular sub-pool of complex-bound non haem iron, and inorganic iron. The bioavailability of calcium from small fish is as high as that from milk, therefore, a major contributor to micronutrient intake (Belton, 2011).

Contamination of fish by heavy metals poses a health risk to the fish consumers, as they are likely to cause detrimental health effects (Kurland *et al*, 2001; Alo, 2006). Olaifa *et al* (2004), acknowledge that roles and fate of heavy metal contamination of fish is a potential health problem to man. Various studies have recorded very high concentrations of heavy metals in fish tissues which are beyond the FAO and WHO limit (Obasohan, 2007; Babatunde *et al*, 2012)

2.6 Conceptual framework

Various heavy metals are accumulated in fish body in different amounts mainly depending on heavy metal bioavailability, fish feeding ecology and other environmental factors (Ishaq, 2011). Further, the differences may result from different affinity of metals to fish tissues, different uptake, and deposition and excretion rates. Metal levels in live fish usually follow the ranking: Fe > Zn > Pb > Cu > Cd > Hg (Obasohan, 2007). Environmental factors such as temperature affect the rate of uptake and accumulation of metals in fish. Heavy metals have high uptake rates with high water temperature because of higher metabolic rate, increasing the rate of metal uptake and binding. Water pH also affects heavy metal accumulation with high accumulation in acidic than alkaline water (Olaifa *et al*, 2004).

Fish feeding behavior also affects heavy metal accumulation in fish tissues. Predatory fish feeding on small fish and zooplanktons accumulate more metals than non-predatory fish and benthivores feeding mostly on phytoplanktons. A fish feeding on specific materials only will concentrate high levels of heavy metals than a fish that has a generalized feeding habit (Jezierska, 2006; Taweel, 2011; Matasin, 2011).

Anthropogenic activities increase the concentration of heavy metals in water bodies. These activities include agriculture and deforestation. Agricultural activities involve use of various agrochemicals (such as pesticides and herbicides) and fertilizers which contain various heavy metals (Hickley *et al*., 2004). Through agricultural run-off, the heavy metals end up in water bodies. Forests are known to reduce water velocity, increase infiltration and therefore reducing the amount of contaminants reaching adjacent water bodies. Deforestation will therefore increase heavy metal concentration in surface waters including lakes (Campbell *et al*, 2003; Alo, 2006). Environmental pollution especially by plastics, metals, oils, pharmaceutical equipments, batteries and mineral tailings contribute to heavy metals pollution of surface waters via surface run-off. Waste disposal methods such as use of incinerators also contribute to high levels of non point heavy metal pollution (Forster. & Wittmann, 1981). Finally, environmental policies aimed at environmental conservation through afforestation, proper solid waste disposal, management of sewage and protection of catchment areas result into a reduction in water pollution and hence reduction of heavy metal contamination in lakes (Farkas & Adelowo, 2007).

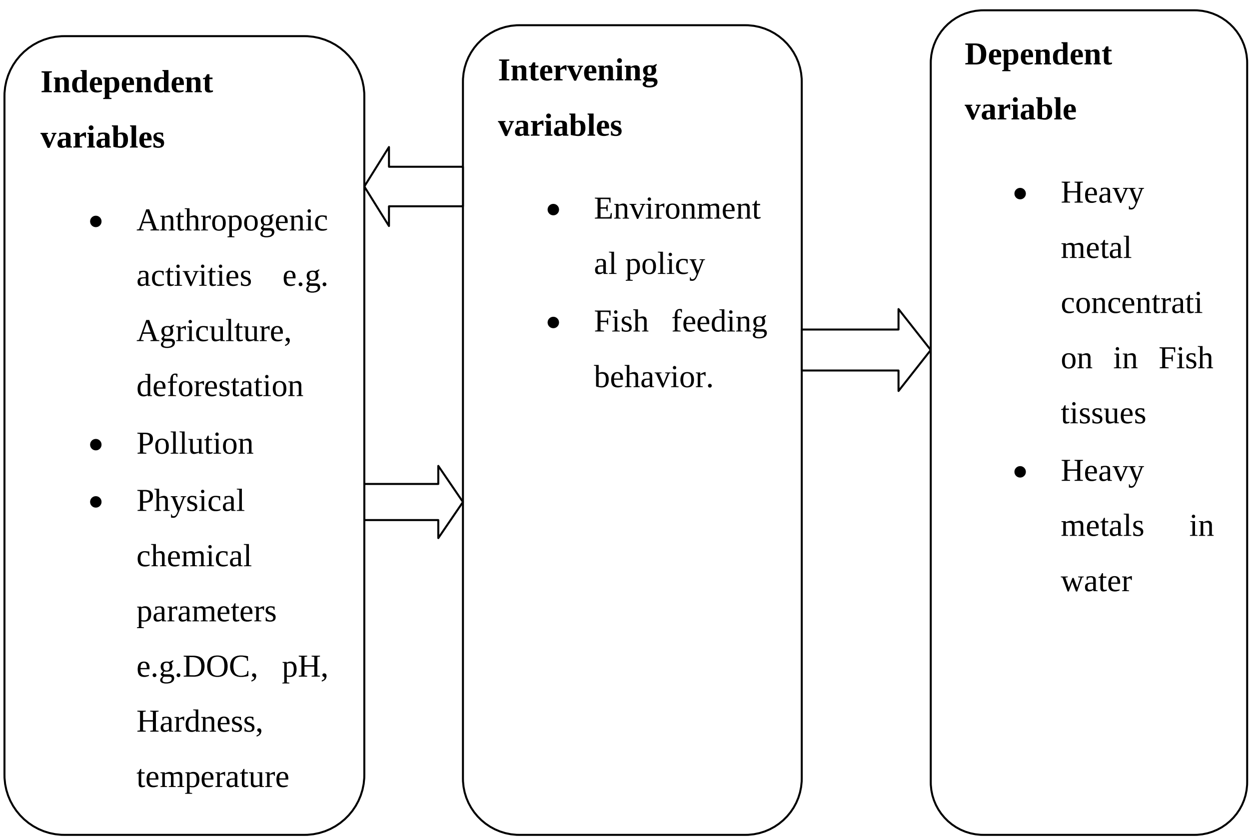


Figure 1: Conceptual framework showing how the study variables are related.

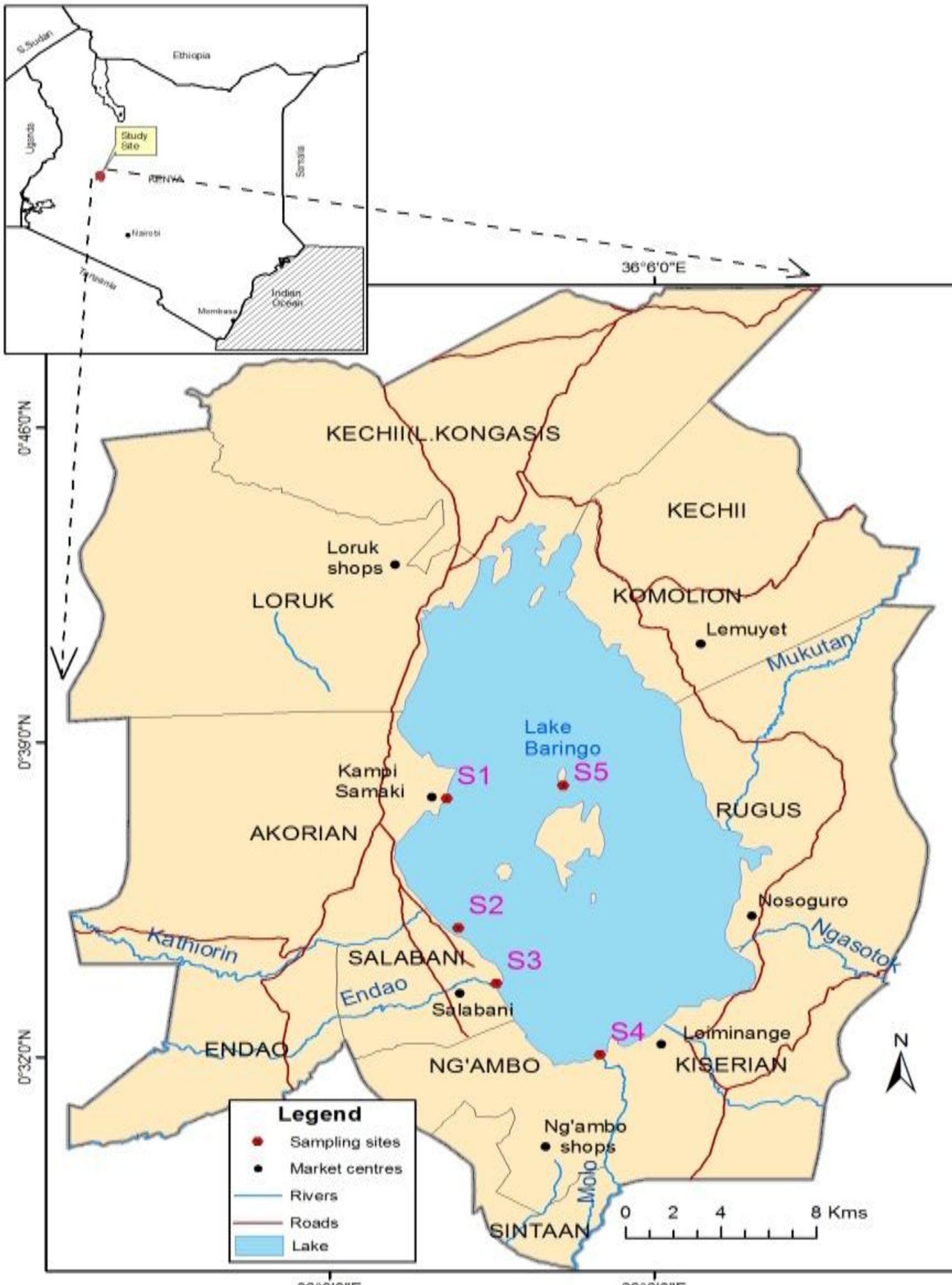
CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study Area

Lake Baringo is a fresh water Lake located in Baringo County in the Rift Valley (fig. 1).It is about 150 km north of Nakuru town at 0°38′N 36°05′E, and the nearest town to the lake is Kampi ya Samaki, which is a small settlement on the western shore of the lake. The Lake is served by two permanent rivers which are Molo and Perkerra and seasonal rivers include Dau, Mugurn, Makutan, Ol Arabel, Tangulbei, Endao and Chemeron and Waseges (Odada, 2005). The lake is fed through inflows from the Mau Hills and Tugen Hills. Lake Baringo has a surface area of about 130 km^2 which may rise to 168 km^2 during the rainy seasons and an altitude of about 1100 m and is surrounded by mountains rising to almost 3000 meters above the ambient ground level in places. The most conspicuous feature of Lake Baringo is its extreme turbidity which is mainly due to soil erosion which results from low vegetation cover, caused by deforestation and overgrazing, exacerbated by high intensity, sporadic rainfall on steep slopes (Campbell *et al*, 2003).

Communities living within the basin of the Lake Baringo (Tugens, Pokots and Illchamus) depend on it as a source of water for various purposes. Livestock over-grazing is a major problem in this area as it increases soil erosion thereby leading to high rates of sedimentation in the lake. Socioeconomic factors also have had both direct and indirect impacts on the lake. These include the increasing demands for development and use of lake resources such as fish, water and tourist facilities and the poor land management with cultivation of river banks and steep slopes without adequate conservation measures (Britton *et al*, 2008).



Ethiopia
S.Sudan
Uganda
Somalia
Study Site
KENYA
Nairobi
Tanzania
Mombasa
Indian Ocean
36°6'0"E
0°46'0"N
0°39'0"N
0°32'0"N
36°0'0"E
KECHII(L.KONGASIS
KECHII
Loruk shops
LORUK
KOMOLION
Lemuyet
Mukutan
Lake Baringo
Kampi Samaki
S1
S5
AKORIAN
RUGUS
S2
Nosoguro
Ngasotok
Kathiorin
SALABANI
S3
Endao
Salabani
S4
Leiminange
ENDAO
NG'AMBO
KISERIAN
N
Legend
Sampling sites
Market centres
Rivers
Roads
Lake
Ng'ambo shops
Molo
SINTAAN
0 2 4 8 Kms

Figure 2: The study area map showing water and fish sampling sites (S1-Kampi ya Samaki discharge point; S2-Endau River discharge point; S3-Salabani discharge point; S4-Molo River discharge point, and; S5-Ol-Kokwar). (Map produced by Geoffrey Maina)

3.2 Study Design

The study was an ecological survey involving determination of the concentration of heavy metals in water and fish in Lake Baringo. Analysis of data was done in order to understand, interpret and make informed decisions to safeguard human health.

3.2.1 Sampling Sites and Sample Collection

Sampling sites were purposefully selected based on the research objectives. As such, sites receiving effluents from the watershed (i.e. one at Molo River mouth, one at Endau River, one at Salabani River, and one at Kampi ya Samaki and Ol Kokwar) were chosen. The estuaries were chosen due to their high level of nutrients and productivity hence fish are abundant. Two replicate water and samples were collected from each of the five sampling sites during each sampling occasion. Samples were collected in, September 2013 and January and twice in June 2014. Therefore, a total of 40 samples of water (2 replicates X 5 sites X 4 sampling occasions) were collected by the end of the study.

3.2.2 Determination of pH, Temperature, Conductivity, and Dissolved Oxygen in water

All the selected physical and chemical variables affecting water quality were determined following methods described in American Public Health Association (American Public Health Association, 1998). Water pH was determined at the sites of sample collection. The pH was measured using a field pH meter and a glass electrode that was standardized immediately before each reading. Conductivity in microsiemens per centimeter (μS/cm) was measured using YSI conductivity meter. The instrument was calibrated before use in the field. The values of conductivity were reported as conductivity of water at 25° C. Temperature and conductivity were determined using YSI conductivity/DO/temperature meter Model 85 (Yellow Springs Instrument Co. Inc. OH, USA).

3.2.3 Analysis of Heavy Metal in Water Samples

Water samples were collected using trace metal clean procedures (Shelton, 1994; Shafer, 1997; American Public Health Association, 1998). All equipment used for sample collection, storage and analysis of heavy metals were pre-cleaned using high-purity nitric acid and rinsed with copious amounts of Milli-Q water to ensure that they were trace-metal free. After rinsing, the bottles were stored in double-bagged zip-lock polyethylene bags. Such cleaning and storage procedures ensured that there were no detectable metal contaminants in the sampling equipment (Shafer, 1997).The samples were collected in polypropylene bottles and filtered immediately through 0.45 µm and acidified with ultra-pure HNO_3 to pH < 2 and stored at 4^oC prior to heavy metal analyses. Other water quality physic-chemical variables known to affect dissolved metals were measured (i.e. dissolved oxygen, pH, electrical conductivity) in the field. Heavy metals in the filtrate (0.45 µm) were operationally defined as "dissolved". Dissolved fraction was focused on as this fraction is more likely to have measurable biological effects on aquatic organisms. In addition, the dissolved metals have been shown to be similar to the exposure conditions used in toxicity tests (EPA, 2002).

Metal concentrations were determined by the Atomic Absorption Spectrophotometer (AAS). In brief, 15 mL of sample was transferred into a vial into which an internal standard containing 40 ug/L ^{6}Li, ^{75}Ge, ^{115}In, and ^{209}Bi was added. 40 ug/L of ^{196}Au was added to the sample solutions to stabilize Hg. A standard calibration curve for all the analytes was established on standards prepared in a linear range from 1 ppb to 100 ppb. National Institute of Standards and Testing Reference material (NIST 1640) and procedural blanks was analyzed for all selected heavy metals.

3.2.4 Fish Sampling and Analysis for Heavy Metals

A total of 40 samples of fish (2 replicates X 5 sites X 4 sampling occasions) were collected for each species by the end of the study. Thereafter, a 50-g sample of muscle tissue from each fish sample was processed according to methods described in Campbell *et al*, (2003). Samples were wrapped in Aluminium foil and stored on ice until transfer to a freezer and later on heavy metal analyses on the fish samples was performed in a clean-room laboratory at the Nakuru Water and Sewerage Company, Water Quality Laboratory, Nakuru, Kenya.

Heavy metals in fish tissue were determined by digesting 50 mg of sample in ultra-pure nitric acid (HNO_3) and hydrofluoric acid (HF) and brought to a final volume of 100 mL in 2% ultrapure HNO_3. Metal concentrations in the fish samples were measured using the atomic absorption spectrophotometer. Standards were prepared in a linear range from 1 μg/L to 1000 mg/L. An internal standard consisting of Li-6, Ge, In, Tm, and Bi was added to each fish sample and external standard. To ensure quality control and assurance, procedural blanks and analytical reference materials USGS-SDO-1 and USGS-SGR-1 were analyzed. All equipment and glassware used in fish sample processing was HNO_3 washed, and rinsed using Milli Q water.

3.2.5 Data Analysis

Descriptive statistics of all the data was calculated and tested for normality using Kolmogorov-smirnov normality test giving $p>0.05$. Heavy metal concentrations in water and fish samples from the selected study sites was compared using analysis of variance (ANOVA) to test for differences among fish species and sites. The criterion for significance was a *p-value* of 5 percent (0.05).

Table 1: Summary of the data analysis techniques

Objectives	Research Questions	Variables	Statistical tools
To determine the physical chemical parameters (pH, temperature, conductivity, dissolved solids and salinity) affecting water quality in Lake Baringo.	Is there is any variation in physical chemical parameters in Lake Baringo?	pH, Temperature, dissolved solids, salinity and conductivity	Descriptive statistics (mean ± SE) ANOVA
2. To determine the concentrations of selected heavy metals (Copper, Mercury, Cadmium and Lead) in water samples taken from different sampling points in Lake Baringo.	Is there significant difference in concentrations of selected heavy metals in water samples collected from different sites in Lake Baringo?	Copper, Mercury, cadmium and lead concentration in water samples	Descriptive statistics (mean ± SE) ANOVA
3. To determine the concentrations of the selected heavy metals (Copper, Mercury, Cadmium and Lead) in the tissues of important commercial fish species (*Oreochromis niloticus baringoensis, Protopterus aethiopicus, Clarias gariepinus)* of Lake Baringo.	Is there variation in concentrations of selected heavy metals in tissues of the selected fish species obtained from Lake Baringo?	Copper, Lead, Mercury and cadmium concentration in fish samples	Descriptive statistics (mean ± SE) ANOVA

CHAPTER FOUR

4.0 RESULTS

4.1 Physical-chemical variables and heavy metal concentration in water samples collected from various sampling sites in Lake Baringo.

The mean values of physical-chemical variables representing the limnological parameters in the water samples from the five sampling sites in Lake Baringo are presented in Table 2.

Table 2: Means (±SE) of various physical-chemical variables in water samples collected from various sampling sites in Lake Baringo.

SITE	*Conductivity (µsm/cm)*	*Water temperature (°c)*	*Air Temperature (°c)*	*Total Dissolved Solids (mg/l)*	*Salinity (mg/l)*	*PH*
Kampi Samaki	370.1±0.67	29.16±0.66	35.88±0.79	370.13±0.87	0.1	8.09±0.13
Endau River	371.8±1.52	29.28±0.59	39.63±1.64	372.13±1.38	0.1	8.06±0.08
Salabani	375.5±2.14	29.31±0.56	39.13±1.01	375.00±1.97	0.1	8.09±0.09
Molo River	371.5±2.32	29.34±0.49	40.63±0.99	370.63±2.45	0.1	7.10±0.07
Olkokwar	369.6±1.25	29.74±0.40	36.13±1.90	369.50±1.04	0.1	8.24±0.07
F-Values	3.04	1.722	2.93	3.27	0	2.9
P-Values	0.03	0.17	0.03	0.02	0	0.03

Olkokwar recorded the highest water temperature (29.74±0.40) while Kampi Samaki recorded the lowest water temperature (29.16±0.66). Air temperature was high at Molo River and lowest at Kampi Samaki. The highest pH value (8.24±0.07) was recorded at Olkokwar and the lowest (7.10±0.07) recorded at Molo River. Salinity was low at 0.1 mg/l in all sites. Total dissolved solids ranged from 375.00±1.97recoreded at Salabani to 369.50±1.04 recorded at Olkokwar. Conductivity was highest at Salabani at 375.5±2.14 and lowest at Olkokwar at 369±1.25.

Table 3: Heavy metal concentrations in ppb (mean ±SE) in water samples collected from Lake Baringo.

Sites	Mercury	Copper	Cadmium	Lead
Salabani	0.002±0.001	0.03±0.02	0.03±0.00	<0.026
Olkokwar	0.003±0.002	0.02±0.00	0.03±0.00	<0.026
Kampi Samaki	0.002±0.001	0.03±0.02	0.02±0.00	<0.026
Endau River	0.002±0.001	0.02±0.00	0.03±0.02	<0.026
Molo River	0.001±0.001	0.03±0.00	0.02±0.00	<0.026
WHO guidelines	0.001	0.05	0.10	0.03

Mercury, cadmium and copper were available in measurable quantities in water samples collected from different sites within Lake Baringo. The highest concentration of mercury (0.003±0.002) was recorded at Olkokwar, and the lowest at Molo River as 0.001±0.001 (Table 2). Copper and Cadmium concentration in water ranged from 0.02-0.03 ppm. Lead concentration in water was below the Instrument detection limit (<0.026). There was a no significant difference in cadmium, copper and mercury concentration in water samples collected from different sampling sites within Lake Baringo ($p>0.05$) . The concentration of all the metals recorded in water samples were within WHO guideline values meant for human consumption.

4.2 Heavy metals in fish samples collected from Lake Baringo

The pooled heavy metal concentrations levels recorded in fish for Copper, Cadmium and Zinc was 0.4728±0.12455, 3.565±0.06289 and 24.398±3.26165 (mean ± standard error) respectively. Thus in this study the heavy metal concentrations in fish decreased in the sequence Zinc>Cadmium>copper. Lead and Mercury concentrations were below the limits of instrument detection. There was no significant difference in heavy metal concentration in all the tilapia

(F=0.88, P=0.44), lungfish (F=0.99, P=0.43) and catfish (F=0.09, P=0.70) samples collected from different sampling sites and respectively.

4.2.1 Copper concentration in the three fish species from different sites in Lake Baringo.

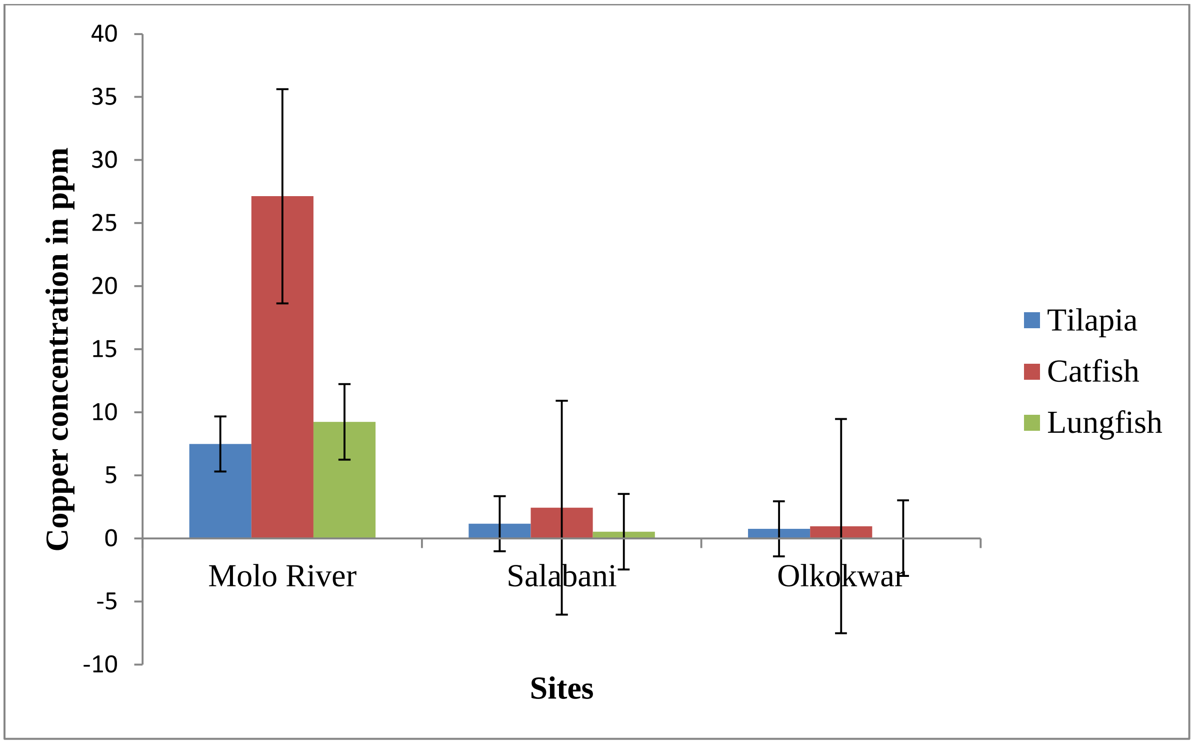


Figure 3: A graph showing Copper concentration in Fish species collected from three sampling sites in Lake Baringo.

Copper concentration in fish ranged from 27.13±0.00 recorded in Molo River to 0.04±0.00 recorded in Olkokwar. The concentration of copper in catfish ranged from 27.13ppm – 0.98ppm. Copper concentration in Tilapia ranged from 7.50ppm – 0.765ppm while in Lungfish, the concentration ranged from 9.26- 0.04ppm. Molo river had the highest copper concentration in the three fish species while Olkokwar had the lowest copper concentration.

4.2.2 Cadmium concentration in the three fish species collected from three sites in Lake Baringo.

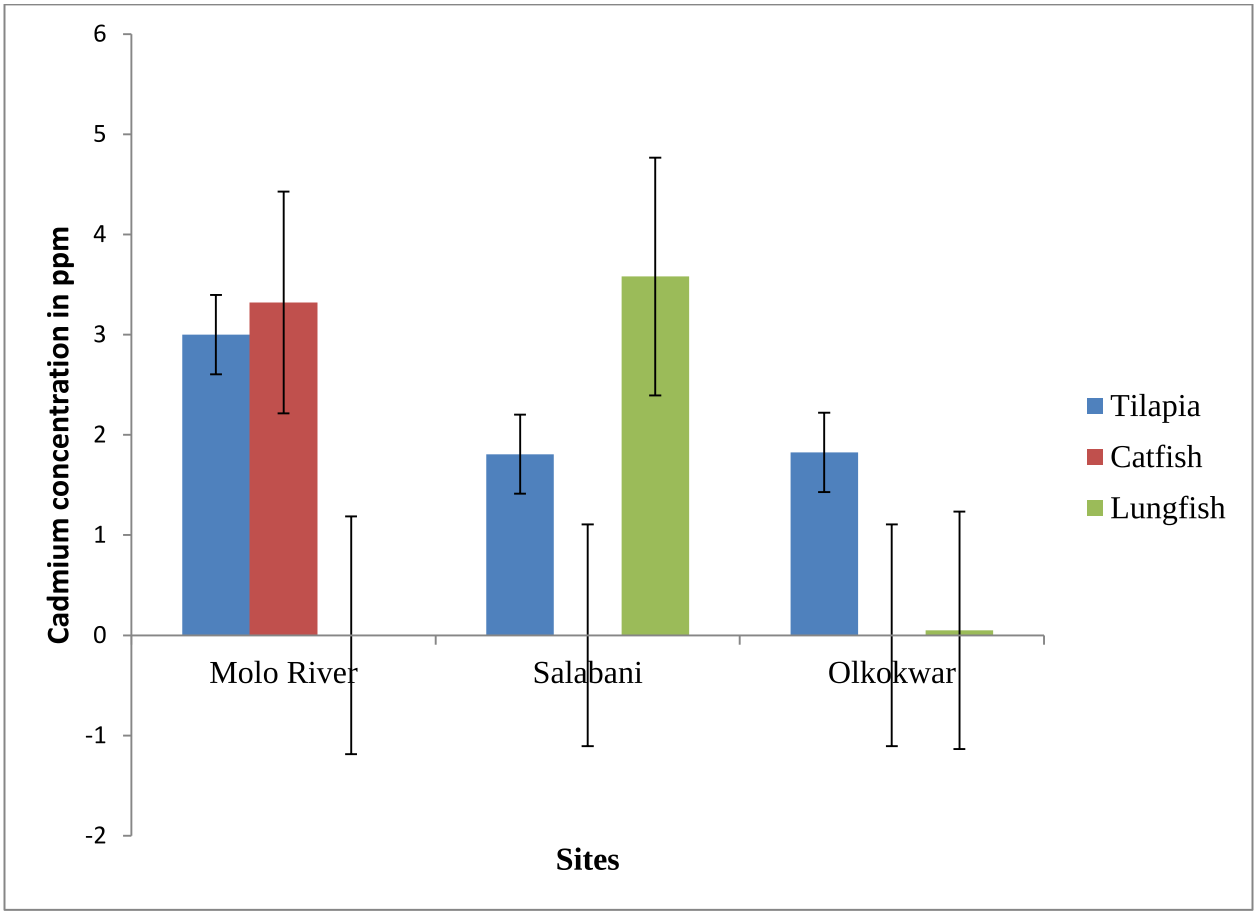


Figure 4: A graph showing Cadmium concentration in Fish species collected from three sampling sites in Lake Baringo.

The highest Cadmium concentration (3.38ppm) was recorded at Salabani and the lowest (0.05ppm) at Olkokwar. Cadmium concentration in catfish was recorded at Molo river (3.32ppm) while in Salabani and Olkokwar, the concentration was below instrument detection (<0.02). Cadmium concentration in Tilapia ranged from 3.0ppm- 1.80ppm and was present in all sites. Cadmium was recorded in lungfish from Salabani (3.38ppm) and Olkokwar (0.05ppm) but was below detection at Molo River.

4.3.3 Zinc concentration in the three fish species collected from three sites in Lake Baringo.

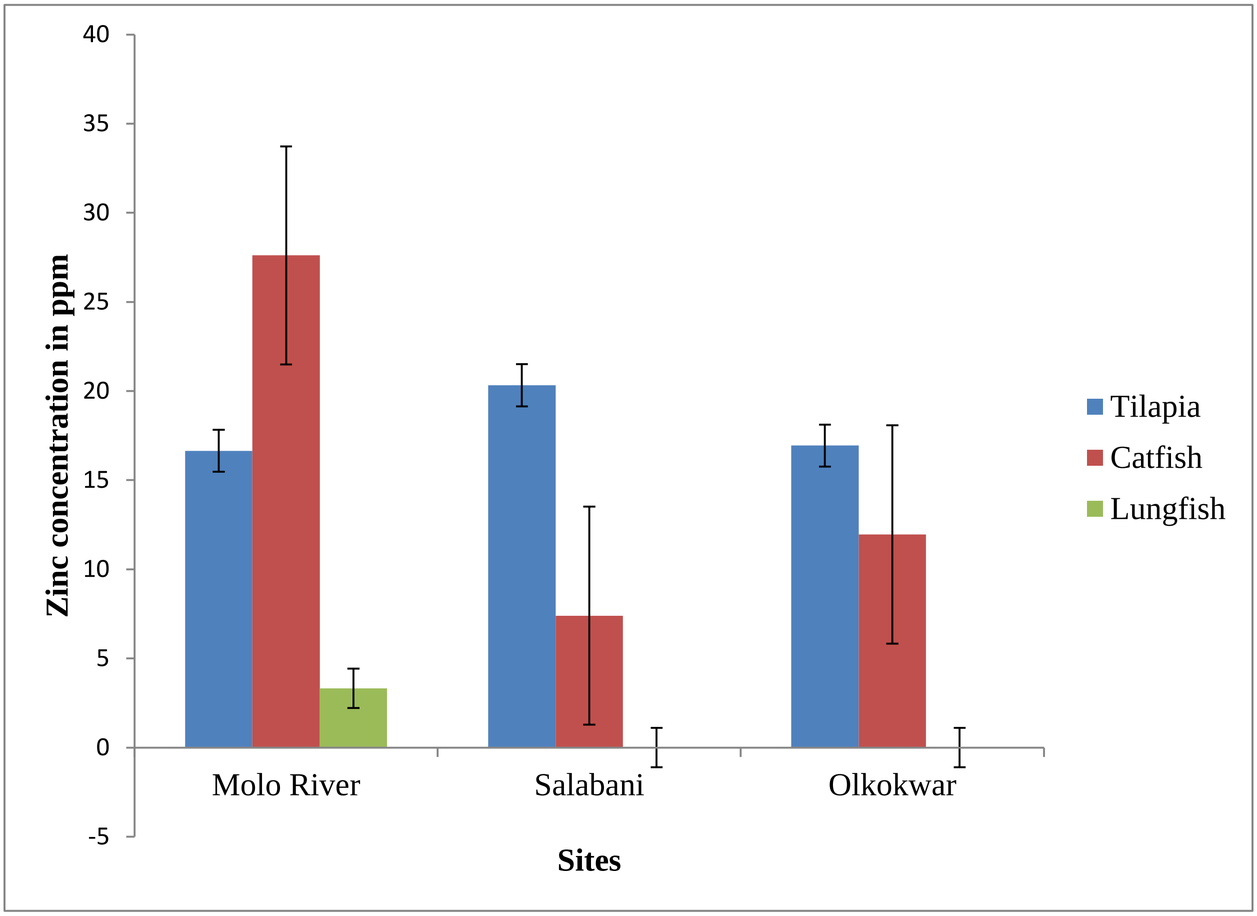


Figure 5: A graph showing Zinc concentration in Fish species collected from three sampling sites in Lake Baringo.

Zinc was the dominant metal with the highest concentration (27.61ppm-3.32ppm) in all fish species. Zinc concentration in Tilapia was high at all the selected sites, that is, Salabani at 20.82ppm, Olkokwar at 16.94ppm and Molo River at 16.65. Zinc was present in catfish in all selected sites at 27.61ppm at Molo River, 7.4ppm at Salabani and 11.95ppm at Olkokwar. However, zinc concentration in Lungfish was only present at fish samples from Molo River and below instrument detection at Salabani and Olkokwar.

CHAPTER 5

5.0 DISCUSSION

5.1 Physical chemical parameters and heavy metal concentration in Lake Baringo water

Physical chemical parameters of a water body influence the rate of heavy metal bioavailability and uptake by living organisms (Lawson, 2011). Knowledge on the physical chemical parameters in aquatic ecosystems is important as these parameters are able to modify heavy metal toxicities. In this study, there was significant difference in conductivity, water temperature, air temperature, total dissolved solids, salinity and pH in water in all sampling sites in Lake Baringo ($p< 0.05$) except for water temperature ($p=0.17$) (Table 1). This can be attributed to the high wave action and stirring of water that is a usual phenomena in Lake Baringo.

Water ph is known to affect heavy metal concentration in aquatic ecosystems by influencing their toxicity and bioavailability. The study recorded low pH values from all sites. Low pH results to high heavy metal toxicity and bioavailability especially Zinc and Cadmium (Heath, 1991). Water pH also affects heavy metal accumulation in living organisms with high accumulation in acidic than alkaline water. Low pH increases free metal ion concentration in water increasing bioavailability of these metals (Al kahtani, 2009). Low pH leads to mercury methylation resulting to formation of Methylmercury which is a very toxic form of mercury. Methylmercury is known to biomagnify along food chains and bioconcentrate in tissues of living organisms (Bacher and Casas, 2006). The study findings agree with this fact in that Molo River that recorded low PH had high heavy metal concentration.

Studies have shown that water temperature influence bioavailability and toxicity of heavy metals with increase in toxicity at high temperatures especially the trace metals (Ochieng *et al*, 2007). The results show high air and water temperature. Heavy metals have high uptake rates with high water temperature because of higher metabolic rate of the organisms, increasing the rate of binding and metal uptake (Olaifa *et al*, 2004). Fish body temperature is the same as that of the surrounding water and therefore there will be increase in metabolic rate with an increase in water temperature. Lead and mercury methylation is dependent on temperature and pH (Lawson, 2011). The study findings agree to this fact as the sampling sites with high temperature also recorded high heavy metal concentration. Odour *et al*, (2003), recorded high solar radiation during the day which results into high water and air temperature.

The study recorded low salinity (0.1mg/l) and conductivity in Lake Baringo. This can be attributed to the fact that Lake Baringo is a closed seepage lake having low conductivity and salinity (Muiruri, Nyambaka, & Nawiri, 2013). This can also be due to the extensive area and volume of the lake as well as the presence of the carbonate salts (Odada, 2005).

The concentration of mercury, lead, copper and cadmium recorded in water samples from Lake Baringo were within WHO guideline values meant for human consumption (table 3). Similar results were recorded by Ozturk *et al*, in Avsar Dam Lake in Turkey (Ozturk *et al*, 2009). The fairly heavy metal concentration in Lake Baringo water can be attributed to the stirring of the shallow turbid water by the high turbulence. The presence of carbonates and bicarbonates from the geological weathering of the volcanic rocks can also result to the bioavailability these metals (Muiruri, Nyambaka, & Nawiri, 2013).

5.3 Heavy metal concentration in fish samples collected from Lake Baringo.

Heavy metals enter the fish through gills, skin and oral in food and water. In the fish body, the metal is transported through the blood stream and either stored, transformed or eliminated in the liver, kidney or the gills (WHO, 2004). Copper is an essential micronutrient required by organisms for normal metabolic processes (WHO, 2004). Although copper is an essential element in human development of bones and growth, at high doses, copper causes vomiting, diarrhea, nausea and headache while chronic copper toxicity results into gastrointestinal bleeding, haematuria, intravascular haemolysis and acute renal failure (Shaker *et al*, 2008). Copper is a very toxic metal in high concentration (Anim *et al*, 2011). Although Copper is naturally occurring in the ecosystem in trace amounts, the concentration level in fish samples from Lake Baringo does not exceed WHO guideline values (0.473±0.125). The results are in agreement with the findings of the study carried out in Egypt Northern Delta Lake on heavy metals in Oreochromis Niloticus (Shaker and Saeed, 2008).

The main natural source of cadmium into the environment is the earth's crust through weathering of rocks and volcanoes. Cadmium is a well-known human carcinogen and long-term exposure to low levels of cadmium lead to fragile bones harm to the lungs and kidney (Wright and Welbourn, 2002).Cadmium concentration levels recorded ranged from 3.32-3.66ppm with the highest concentration recorded in Tilapia fish sample from Molo River. Cadmium concentration in fish exceed WHO guideline values (3.565±0.0629). FAO recommends 0.05ppm due to the high toxicity of the metal even at low concentration while WHO gives a guideline value of 0.1ppm. Being one of the main inflow rivers feeding the lake, this high concentration in Molo River can be attributed to anthropogenic input. Similar results were recorded by Mwashote (2003) in a study of Indian Ocean whereby high cadmium levels were recorded at sites impacted by anthropogenic activities.

The high cadmium concentration in fish can be attributed to the high mobility of Cadmium as well as the high temperatures that promote cadmium accumulation in tissues of living organisms. Similar results were recorded at Awassa and Koka Lakes in Ethiopia (Dsikowitzky *et al*, 2012) and (Milan *et al*, 2012).The high cadmium concentrations are a human health concern. There is potential influence of geochemical processes on the concentration values as well as the increase in subsistence, commercial and recreational fishing activities (Tuionen *et al*, 2006). Cadmium is known to have long residence time in kidney and liver and is readily bound to hemoglobin and metallothionein (Njogu *et al*, 2011). Ochieng *et al*, (2007) recorded similar results in lake Baringo.

Zinc concentration recorded in Lake Baringo exceeds WHO a permissible limit of 10mg/kg (figure 4). The study recorded high zinc concentration in fish at 27.61ppm-3.32ppm. Zinc is an essential metal required by living organisms for development and normal growth and can be stored in low to moderate concentration for normal homeostatic functions. However, WHO has classified zinc as a highly toxic metal at high concentrations (Wright and Welbourn, 2002). Zinc plays an important role in living organisms especially in enzymytic processes and hence fish have active uptake and storage of Zinc. Njogu *et al.* 2011 recorded similar results in Lake Naivasha, Kenya. The high zinc concentrations recorded in Lake Baringo can be attributed to increased anthropogenic and agricultural activities around the lake. These activities have increased the release of Zinc from geologic sources becoming bioavailable for fish uptake via diet and water by epidermis and gills. Given the fish position at the high trophic levels, there is a high likelihood of concentrating high levels of zinc especially from dietary exposure.

Mercury is known to permanently damage the kidney, nervous system, developing fetuses and the brain. Mercury has low solubility in water and is known to be liquid at room temperature. Dissolved Mercury occurs in different chemical forms which include the volatile and relatively unreactive form of elemental Hg, ethyl, dimethyl and methyl mercury (Bacher and Casas, 2006). The low mercury levels in water and fish can be attributed to this observation given that some studies have recorded it as high in sediments than in water and fish (Ismaliza and Idaliza, 2012).

Lead concentration in fish was below WHO guideline value and below the instruments lowest limit of detection (<0.026mg/kg). Lead is introduced into the environment from mining, fossil fuel burning, batteries, and pipes, manufacturing activities and burning of fossil fuels. Lead is known to be extremely toxic metal and has been identified as a possible human carcinogen. Long-term exposure to low levels of lead can affect the nervous system, lead to damage to kidneys and brain and damage of the reproductive system (Mansour and Sidky, 2002). Studies have shown that Lead concentration is high in lower food chain components such as zooplanktons and algae but with low biomagnification, the components at upper trophic levels such as fish have low concentration. Lead has low mobility and has high dilution in water and is highly bound to particulates. Therefore Lead has limited bioaccumulation and this explains the low concentration in fish (Ogoyi *et al*, 2011). The results are contrary to the findings by Tole and Shitsama, (2003) on heavy metal concentration in fish, water and sediments from Winam Gulf of Lake Victoria.

The results show that there was no significant difference in the concentration of copper, cadmium and zinc in fish samples (P>0.05). Molo River recorded the highest concentration in Copper and Cadmium levels in the three fish species that exceeded WHO guideline values. This can be attributed to anthropogenic input especially form the agricultural activities at the catchment areas, Molo River being the largest feeder river into the lake. Olkokwar and Salabani recorded low copper values that were below WHO guideline values. However the Cadmium values in the latter sites exceeded WHO guideline values. Salabani recorded the highest Zinc concentration compared to Olkokwar and Molo River. However, the Zinc concentrations in all the three sites exceeded WHO guideline values.

CHAPTER 6

6.0 CONCLUSIONS AND RECCOMMENDATIONS

6.1 Conclusions

The results show that there is variation in physical chemical parameters in water from different sites in Lake Baringo. From above mentioned results, heavy metal concentration in water from Lake Baringo is below WHO guideline values and hence posing an environmental rather than human health concern. It is clear that the concentration of zinc and cadmium in fish is above WHO guideline values therefore poses a human health concern. However, copper concentration poses more of environmental than human health concerns. Therefore efforts should be taken to reduce pollution in Lake Baringo. The results also show that sampling sites with high water temperature and low pH recorded high heavy metal concentrations.

6.2 Recommendations

(1) Further studies on guidelines for safe fish consumption quantities/ intakes as well as the sources of the heavy metals in Lake Baringo are recommended.

(2) Since cadmium and zinc concentration in fish were above the WHO guideline values, there is need to carry out continuous monitoring of contaminants in Lake Baringo and to be able to assess human health risks.

(3) Regular monitoring of the Lake Baringo water quality is needed to record any variation in the quality and alleviate outbreak of heavy-metal related health disorders in ever increasing fish consumers.

(4) This study provides significant data for future research on Lake Baringo such as regular surveillance of pollutants, assessment of consequences of these pollutants on Lake Baringo ecosystem over the long term and heavy metal concentrations in various fish tissues to help issue fish consumption advisories.

REFERENCES

Anim, A.K., Ahialey, E.K., Doudu, M, (2011). Accumulation profile of heavy metal in fish samples from Nsawam along the Densu River, Ghana. *Research Journal of Environmental and Earth Sciences*. Vol 3. 56-60

Al-Kahtani, M. A. (2009). Accumulation of heavy metal in Tilapia fish(Oreochromis niloticus) from Al-Khadoud Spring Al-Hassa, Saudi Arabia. *American Journal of Applied Sciences* , 2024-2029.

Alo, B. (2006). *Heavy Metal Pollution in Different Environmental Media in Africa. Problems and Prospects(with case studies from Nigeria).* Abuja: University of Lagos Centre for Environmental Human Resources Development Department of Chemistry.

American Public Health Association, A. (1998). *Standard methods for the examination of waste water.* Washington DC: APHA.

Babatunde, A., Oyebanjo, W., & Adeolu, A. (2012). Bioaccumulation of heavy matals in fish (Hydrocynus forskahlii, Hyperropiusus bebe,Occidentalis and Clarias gariepinus) organs in downstream Ogun Coastal Water, Nigeria. *Transnational Journal of Science and Technology* .vol 2 123-127

Belton, B. (2011). *Review ofAquaculture and Fish Consumption in Bangladesh.* Malaysia: WorldFish Center.

Bezuidehout. L. M, Schoonbee., H. J, & Dewet, L. (1990). Heavy metal content in organs of the African Sharptooth Catfish, Clarias gariepinus; Burchel from a transvaal lake affected by mine and industrial effluents. Part 1. *Water South Africa* , 125-129. vol. 16

Berg., H., Kiibus., M., & Kautsky, N. (1995). Heavy metals in a tropical Lake Kariba Zimbabwe. *Water and Soil Pollution* , 237-252.

Britton, A., Jackson, C., & Muchiri, M. (2008). *Status, Ecology and Conservation of an Endemic fish (Oreochromis niloticus baringoensis) in Lake Baringo, Kenya.* London: John Wiley and Sons.

Cedric., B. (2006). Modeling trace metal (Hg and Pb) bioaccumulation in the mediterranean mussel, Mytilus galloprovincialis. *Journal of sea Research* , 168-181.

Campbell, L., Osano, O., Hecky, O., & Dixon, G. (2003). Mercury in fish from three rift valley lakes (Turkana,Naivasha and Baringo), Kenya, East Africa. *Environmental Pollution* , 281–286.

Dsikowitzky., L., Mengesha., M., Dadebo., E., Eduardo., C., Calvalho., V. d., & Sindern, S. (2012). Assessment of heavy metals in water samples and in fish tissues of edible fish species from Awassa and Koka Rift Valley Lakes, Ethiopia. *Environmental Monitoring and Assessment* .

EPA. (2000). *EPA's Terms of Environment.* U.S. Environmental Protection.

Evangelou, V. P. (1998). *Environmental Soil and Water Chemistry; Principles and applications.* Toronto: John Wiley & Sons, Inc.

Farkas, E., & Adelowo, O. (2007). Biomarkers of oxidative stress and heavy metal levels as indicators of environmental pollution in African Cat fish (Clarias gariepinus) from Nigeria Ogu river. *International journal of environmental resources and public health* , 158-165.

Flavo, C. (2008). *Lead and Cadmium: Need for International Action?* The Center for International Environmental Law (CIEL).

FAO. 2012. *The State of World Fisheries and Aquaculture* (2012). Food and Agriculture Organization of the United Nations. Fisheries and Aquaculture Department. Rome, Italy.

Food and Agriculture Organization, FAO. (2010, January 1). *Cultured Aquatic Species Information Programme*. Retrieved May 3, 2013, from FAO 2010-2013: http://www.fao.org/fishery/culturedspecies/clarias_gariepinus/en

Forster., U., & Wittmann, G. (1981). *Metal Pollution on the Aquatic Environment.* New York: Spring-Verlang Berlin.

Giordano, R., Arata, P., Ciaralli, L., Rinaldi, S., Giani, M., Cicero, M.A. and Costantini, S. (1991) Heavymetals in mussels and fish from Italian coastal waters. *Mar. Poll. Bull.* **22:** 10–14.

Griesbauer, L. (2007). *Methylmercury Contamination in Fish and Shell Fish.* CSA discoverly guides.

He, Z. Z. (2007). Analysis of Heavy Metals of Muscle and Intestine Tissue in Fish – in Banan Section of Chongqing from Three Gorges Reservoir, China. *Polish Journal of Environmental Studies* , 949-958.

Heath, A. G. (1991). *Water Pollution and fish physiology.* Florida USA: Lewis Publishers.

Hickley, P., Muchiri, M., Boar, R., Britton, C., Adams, C., Gichuru, N., et al. (2004). Habitat degradation and subsequent fishery collapse in Lakes Naivasha and Baringo, Kenya. *Ecohydrology and Hydrobiology* , vol 4. 503-517.

Holister, G., & Porteous, A. (1976). *The Environment: A Dictionary of the World Around Us.* London: Arrow.

Hu, H. (2002). Human Health And Heavy Metals Exposure. In M. McCally, *Life Support: The Environment and Human Health.* MIT press.

Ishaq, E. (2011). Bioaccumulation of Heavy Metals in Fish (Tilapia Zilli and Clarias Gariepinus) Organs from River Benue,North – Central Nigeria. *Pakistan Journal of Analytical Environmental Chemistry.* , 25-31.

Jezierska, B. (2006). The Metal Uptake and Accumulation in Fish Living in Polluted Waters. *Soil and Water Pollution Monitoring, Protection and Remediation.* , 3-23.

Kariman, A., Shallof, S., & Nehad, K. (2009). Stomach contents and Feeding Habits of Oreochromis niloticus from Abu-Zabal Lakes, Egypt. *World Applied Sciences Journal* , 01-05.

Kees, G., & Frans, W. (2002). Decline of the African Lungfish (protopterus aethiopicus) in Lake Victoria (East Africa). *African Journal of Ecology* , 42-52.

Kurland., T., S.Faro, & Siedler, H. (2001). Minamata Disease; The outbreak of a neurological Disorder in Minamata Japan and its relation to ingestion of sea food containing Mercury compounds. *World neurological Journal* , 370-395.

Lawson, E. O. (2011). Physico-chemical parameters and heavy metal contents of water from the Mangrove Swamps of Lagos Lagoon, Lagos Nigeria. *Advances in Biological Research* , vol 5. 8-25.

Mansour S.A. and Sidky M.M. (2002). Ecotoxicological Studies: Heavy Metals Contaminating Water and Fish from Fayum Governorate, Egypt," *Food Chemistry,* Vol. 78, No. 1, 2002, pp. 15-22.

Matasin, Z. (2011). Heavy Metal Concentrations in Predator Fish. *Journal of Animal and Veterinary Advances* , 1214-1218.

Merriam. (1976). *3rd New International Dictionary.* Chicago: Merriam.

Milan, C., H., M. M., L., U., & Ozoemena, P. (2012). Heavy metal pollution in benthic fishes from Kiri Dam in Guyuk local goverment area of Adamawa State, Nigeria. *African Journal of Biotechnology* , 11755-11759.

Mozaffarian, D. (2006). Fish Intake, Contaminants, and Human Health:Evaluating the Risks and the Benefits. *Journal of American Medical Association* , 1885-1899.

Muiruri, J., Nyambaka, H. N., & Nawiri, M. P. (2013). Heavy metals in water and tilapia fish from Athi-Galana-Sabaki tributaries, Kenya. *International Food Research Journal* , 891-896.

Muiruri., J., Nyambaka., H., & Nawiri, M. (2013). Heavy metals in Water and Tilapia Fish from Athi-Galana-Sabaki Tributaries, Kenya. *International Food Research Journal* , 891-896.

Museum, M. (2007). *Minamata Disease: Its History and Lessons.* Minamata City: Minamata City Planning Division.

Mwashote, B. M. (2003). Levels of Cadmium and Lead in Water, Sediments and Selected Fish Species in Mombasa, Kenya. *Western Indian Ocean Journal* , 25–34.

Nemr, A. E. (2003). Concentration of certain heavy metals in imported frozen fish in Egypt. *Egypt Journal of Aquatic Biology and Fish* , 139-154.

NJDEP. (2012). *Fish Smart, Eat Smart: A guide to Health Advisories for Eating Fish and Crabs Caught in New Jersey Waters.* New Jersey: New Jersey Department of Environmental protection.

Njogu., P., J.M.Keriko., R.N.Wanjau., & J.J.kitetu. (2011). Distribution of heavy metals in various lake matrices: water,soil,fish and sediments: A case study of the Lake Naivasha basin, Kenya. *Jomo Kenyatta University of Ariculture Science and Technology* , 23-47.

Obasohan, E. (2007). Heavy metals concentration in the Offal, gill, muscle and liver of fresh water mudfish (Parachama obscura) from Ogha River, Benin City, Nigeria. *African Journal of Biotechnology* , 2626-2629.

Ochieng', E.Z,.Halah, J.O,. Wandiga, S.O. (2007). Analysis of heavy metal and surface sediments in five Rift Valley Lakes in Kenya for Assessment of recent increase in anthropogenic activities. Bulleting on environmental contamination and toxicology. vol 79. 570-576

Odada, E. (2005). *IW: LEARN*. Retrieved JANUARY 11, 2013, from www.iwlearn.net/publications: iwlearn.net

Oduor S.O.,Schager M., Mathooko J.M. (2003). On the limnology of Lake Baringo (Kenya). Temporal Physico-chemical dynamics.*Hydrobiologia*, 506-509. 121-127

Ogoyi, D. O., C.J.Mwita, Nguu, E., & P.M.Shiundu. (2011). Determination of heavy metal content in water, sediments and microalgae from Lake Victoria. *The open Environmental Engineering Journal* , 156-161.

Olaifa., F., Adelaja., A., Olaifa., A., & Owolabi, A. (2004). Heavy metal contamination of Clarias gariepinus from a lake and fish farm in Ibadan, Nigeria. *African Journal of Biomedical Research* , 145-148.

Ozturk., M., Ozozen., G., Minareshi., O., & Minareshi, E. (2009). Determination of heavy metals in fish, water and sediments of Avsar Dam Lake. *Iran Journal of Environmental Health, Science and Engineering* , 73-80.

Rasheed, M. (2008). Monitoring of Heavy metals in fish from Nasser Lake. *Environmental International Journal* , 168-175.

Safahieh, A. (2011). Heavy Metal Concentration in Belangers Croaker Fish, Johnius belangerii from petrochemicals waste receiving estury in Persian Gulf, Iran. *Environmental Engineering and Applications.* Khorramshahr : IACSIT press.

Santos, E. (2010). Identifying Health Impacts of Exposure to Copper Using Transcriptomics and Metabolism in a Fish Model. *Environmental Science And Technology* , 820-826.

Schmitt., C., Whyte., J., Biumbaugh., W., & Tillitt, D. (2005). Biochemical Effects of Lead, Zinc and Cadmiumfrom mining on fish in the Tri-states District of Northeastern OKlahoma USA. *Environmental Toxicology and Chemistry* , 1483-1495.

Shafer, M. M. (1997). The influence of dissolved organic carbon, suspended particulates and hydrology on the concentration partitioning and variability of trace metals in two contrasting Wisconsin watersheds. *Journal of chemical geology* , 136:71-97.

Shaker, I. M., & Saeed, S. M. (2008). Assessment of heavy metal pollution in water and sediments and their effect on Oreochromis Niloticus in Northern Delta Lakes, Egypt. *8th*

International Symposium on Tilapia in Aquaculture (pp. 475-490). Egypt: Central Laboratory for aquaculture Research, Agricultural Research Centre.

Shinn, C. (2009). Temporal variation of heavy metal contamination in fish of the river lot in southern France. *Ecotoxicology and Environmental Safety* , 1957–1965.

Shrivastava, V. S. (2011). Study for Determination of Heavy Metals in Fish Species of the River Yamuna (Delhi) by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). *Advances in Applied Science Research* , 161-166.

Storelli, M. (2008). *Potential human health risks from metals (Hg, Cd, and Pb) and polychlorinated biphenyls (PCBs) via seafood consumption: Estimation of target hazard quotients (THQs) and toxic equivalents (TEQs).* Valenzano, BA, Italy: Pharmacological-Biological Department,University of Bari.

Taweel, A. (2011). Heavy metals concentration in different organs of tilapia fish (Oreochromis niloticus) from selected areas of Bangi, Selangor, Malaysia. *African Journal of Biotechnology* Vol. 10 , 11562-11566.

Tole., M. P., & Shitsama, J. M. (2003). Concentrations of heavy metals in water, fish and sediments of the Winam Gulf Lake Victoria Kenya. *Aquatic Ecosystem Health and Management Society* , 1-9.

Tuionen., T., Pihlstrom., M., Arvola., L., & Rask, M. (2006). Concentration of heavy metals in food web components of small boreal lakes. *Boreal Environmental Research* , 183-194.

US Environmental Protection Agency, U. (2002). *Short-term Methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms.* Washington DC: USEPA.

USEPA. (2000). *Methods for Measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates.* washington DC: Office of Research and Development.

Vijayakumar, P. (2011). Heavy Metal Concentration In Three Commercial Fish Species in Cuddalore Coast, Tamil, Nadu, India. *Journal of Environmental Sciences* , 2218-1768.

Welbourn, D. W. (2002). *Environmental Toxicology.* Cambrige UK: Cambrige University Press.

WHO. (2004). *Copper in Drinking Water. Background Document for the Development of WHO Guidelines for Drinking Water Quality.* Geneva: WHO.

WHO. (2010). *Preventing Disease Through Healthy Environments; Exposure To Cadmium: A Major Public Health Concern.* Geneva: WHO.

WHO. (2010). *Preventing Disease Through Healthy Environments;Exposure to Lead. A Major Public Health Concern.* Geneva: WHO.

zheng Zhang & Li He. (2007). Analysis of Heavy Metals of Muscle and Intestine Tissue in Fish – in Banan Section of Chongqing from Three Gorges Reservoir, China. *Polish Journal of Environmental Studies* , vol 16: 949-958.