ASSESSMENT OF HEAVY METAL CONTAMINATION IN MASINGA RESERVOIR, KENYA

By

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DECLARATION

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This thesis is my original work and has not been presented for a degree or award in any other university.

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DEDICATION

To my dear wife Emily, daughter Joy and my son Victor: To my mother Mrs. Rebecca K. Nzeve: you laid a good educational foundation in my life.

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LIST OF ABBREVIATIONS AND ACROYNMS

AAS	Atomic Absorption Spectrometer
ANOVA	Analysis of Variance
APHA	American Public Health Association
ATSDR	Agency for Toxic Subsatances and Disease Registry
BMU	Beach Manangement Unit
DO	Dissolved Oxygen
EC	Electrical Conductivity
EPA	Environmental Protection Agency
FAO	Food Agricultural Organization
GOK	Government of Kenya
KMFRI	Kenya Marine Fisheries Research Institute
NEMA	National Environmental Managemnet Authority
NRM	Natural Resources Management
StDev	Standard Deviation
TARDA	Tana and Athi River Developmnet Authority
TF	Transfer Factor
UN	United Nations
UNEP	United Nations Environmental Programme
USA	United States of America
WARMA	Water Resources Management Authority
WHO	World Health Organization

ABSTRACT

In Kenya, monitoring of heavy metal pollution is a priority area of research since their concentrations in aquatic ecosystems affect the fish industry which is a major source of livelihood. Therefore, an assessment of heavy metal contamination (Cu, Zn, Pb, Cr, Mn and Cd) in sediments, water and in three selected fish species (*Cyprinus carpio*, *Clarius gariepinus* and *Oreochromis spirulus niger)* in Masinga reservoir was carried out between January and December 2013 in five sampling sites. Physical parameters (water temperature, dissolved oxygen, pH, turbidity and electrical conductivity) were measured on site. Heavy metal Concentrations were determined using atomic absorption spectrophotometry. The data obtained was analyzed using one way analysis of variance and significant differences accepted at $p \leq 0.05$. Tukey's HSD test was used to separate means. The mean values for the physical parameters ranged from 24.93 – 27.53^{0}C (water temperature), 4.66 - 5.36 mgL^{-1}(DO), 41.50 – 64.23NTU (Turbidity), 109.79 – 125.98µS cm^{-1} (EC) and 7.51 – 7.88 (pH). The results revealed significant difference only in water temperature ($p = 0.044$). Mean heavy metal concentrations (mg kg^{-1}) in sediments were Cu (11.38 – 23.67), Zn (60.04 – 75.84), Pb (11.14 – 14.47), Cr (21.39-49.62) and Mn (259.12 – 642.30). There were significant differences in metal concentrations for Cu ($p = 0.00$), Cr ($p=0.00$) and Mn ($p=0.00$) among the sites. Surface water from different sites did not show significant differences in heavy metal contamination ($p > 0.05$). The mean metal levels (mg kg^{-1}) in *Cyprinus carpio* muscle tissues were in the range of Cu (0.519 – 1.422), Zn (39.466 – 62.233), Pb (0.994 – 1.424), Cr (0.324 – 0.709) and Mn (0.660 – 1.432). There was significant difference in Zn ($p=0.006$) and Mn ($p=0.001$) in *Cyprinus carpio* muscles at different sites. In *Clarias gariepinus* muscles, mean metal concentrations (mg kg^{-1}) were Cu (0.677 – 0.974), Zn (32.929 – 37.205), Pb (0.643 – 0.078), Cr (0.516 – 0.858) and Mn (0.452 – 0.990). Pb exhibited significance difference between the sites ($p=0.026$). Mean values for heavy metals in Tilapia (mg kg^{-1}) for different sites were Cu (0.515 – 0.782), Zn (29.645 – 37.999), Pb (0.552 – 0.765), Cr (0.559 – 0.791) and Mn (0.183 – 1.480). Only Mn showed significant differences between the sites ($p=0.00$). Pearson matrix correlation analysis showed some significant correlations among the heavy metal levels in water, sediments and different fish species. Bioaccumulation transfer factor (TF) calculated showed that water had higher TF compared to sediments. The concentrations for all metals in surface water did not exceed the WHO recommended limit for drinking water. In sediments and the three fish species they were also lower than WHO set limit except for Cr. Results from this study demonstrate the need for an ecosystem approach towards sustainable management of reservoirs. This will curb aquatic pollution which is a health risk to people consuming aquatic resources contaminated with heavy metals.

CHAPTER ONE: INTRODUCTION

1.1 Background to the Study

Freshwater reservoirs play an important role in the livelihood of human populations. They are used as a source of domestic water supply, irrigation, fishery development, hydropower generation and flood control. Additional benefits of the reservoirs are tourist attraction and opening up of new areas for development (Kitur, 2009). According to Dudgeon (2006) and Junk (2002), freshwater ecosystems are vulnerable to human impacts hence, they are likely to be influenced by reservoir catchment activities. This is because terrestrial ecosystems have linkages with aquatic ecosystems (UNEP, 2000). Contamination of aquatic ecosystems with a wide range of pollutants has become a matter of concern over the past few decades (Dirilgen, 2001; Vutukuru, 2005; Yousafzai and Shakoori, 2008; Narayan and Vinodhini, 2008).

FAO (1992) noted that the contamination of water supplies from both natural and anthropogenic sources has impacted on the health and economic status of populations. Human activities cause pollutants such as heavy metals, pesticides and herbicides to enter aquatic ecosystems. These anthropogenic activities continuously increase the amount of heavy metals in the environment, especially in aquatic ecosystems. Thus, heavy metal pollution is growing at an alarming rate and has become an important worldwide problem (Malik *et al.,* 2010). Increase in population, urbanization, industrialization and agricultural practices as well as

lack of environmental regulations have further aggravated the situation (Gupta *et al.*, 2009).

Heavy metals cannot be degraded but they are deposited, assimilated or incorporated in water, sediments and aquatic biota causing heavy metal pollution in water bodies (Linnik and Zubenko, 2000; Malik *et al*., 2010). Heavy metals in water can originate both from natural sources, industrial, agricultural and domestic activities in the drainage basin of a water system. As the metal levels in many aquatic ecosystems increase due to anthropogenic activities, they raise the concern on metal bioaccumulation through the food chain and related human health hazards (Wright and Welbourn, 2002; Indrajith *et al.*, 2008; Agah *et al*., 2009). Fish being at the top of the aquatic food chain may concentrate large amounts of metals from the water (Mansour and Sidky, 2002). As a consequence, fish are used as indicators of heavy metal contamination in the aquatic ecosystem because they occupy high trophic levels and are important food source (Blasco *et al*., 1998; Agah *et al*., 2009).

In Kenya a number of hydroelectric power generating dams have been constructed along the Tana River since the late 1960's, the largest is Masinga dam which became operational in 1981 (Maingi and Marsh, 2002). Masinga dam has been identified as the most effective regulator of the Tana River system because of its great size and its strategic location in the upper reaches of the system (Pacini *et al*., 1998).

However, unregulated deforestation and expansion of cultivation practices onto marginal soils has resulted in significant reservoir siltation, reduced ecosystem function, and more erratic downstream flows (Jacobs *et al*., 2007). Most of the highland forests of the Tana system occur in the upper Tana catchment above the Masinga dam (Schneider and Brown, 1998). According to Bunyasi *et al.,* (2013), Masinga catchment had lost 62% forest cover (21,180.87 hectares) between the years 1976 and 2011. This has led to increased sedimentation into Masinga reservoir which is estimated at 5.45 million m^3/year (Bunyasi *et al*., 2013) and hence the reservoir has lost 10.1% of its capacity in the last 30 years.

1.2 The Problem Statement and Justification

Increase in pollution of water bodies is directly or indirectly related to increasing urbanization and indiscriminate disposal of agrochemical and industrial effluents into aquatic systems (Dua and Gupta, 2005). In developing countries, trace metal analysis in freshwater is very important because these ecosystems provide drinking water and are habitats for flora and fauna. In Kenya, heavy metal pollution monitoring is a priority area of research since concentrations of heavy metals in aquatic ecosystems affect the fish industry which is a major source of livelihood (Ochieng *et al*., 2008). According to Allinson *et al.,* (2009), fish assimilate metals by ingestion of particulate materials suspended in water, ingestion of food, ion exchange of dissolved metals across lipophilic membranes for example the gills, and adsorption on tissue and membrane surfaces.

Most of the research done in Kenya on heavy metal contaminants has concentrated on lakes and along the coastal-line. A few examples of these studies have been conducted at Lake Victoria (Oyoo - Okoth *et al.*, 2010), satellite lakes within L. Victoria basin (Mwamburi, 2009), Winam Gulf (Lalah *et al*., 2008), Rift valley lakes (Ochieng *et al*., 2007), Lake Naivasha (Kamau *et al*., 2007), fish species in Mombasa (Mwashote, 2003), and Port-Reitz Creek (Kamau, 2002). There is very little research on heavy metal pollution that has been done on reservoirs and especially the ones with fisheries of economic value like the Tana River dams. However, a few ecological studies that have been done on Masinga reservoir include soil and water conservation (Atkin, 1984), impact of dam construction (Rogeri, 1985) and status on Tana River dam fisheries (Dadzie and Odero, 1989). Other studies done are on sedimentation (Maingi, 1991), nutrients (Pacini, 1994), review of Tana River dam fisheries (Knight and Piesold, 1997) and effect of changing water levels on fishes and fisheries (Jumbe, 2003).

Over the years, numerous factors have contributed to the degradation of water resources within the upper Tana catchment. The upper Tana catchment area is characterized by high population densities, rapid urbanization and high agricultural activities (UN-WATER, 2006). The catchment comprises of three river subsystems. These are Tana River which is the largest of the catchment area (91%), Thiba River subsystem (2.8%) and Thika River subsystem (4.2%). The Tana River and Thika River sub basins drain into Masinga reservoir while Thiba sub basin drains into Kamburu dam (UN-WATER, 2006).

Masinga dam has fisheries of economical value. In the year 2012, a total of 608 metric tonnes of fish were landed in four gazetted landing sites (GOK, 2012). This was four times the fish catches got from Lake Naivasha (143 metric tonnes) and two and half times the fish landed from Lake Baringo (250 metric tonnes). The most important species in the catches were Tilapia species (mainly *Oreochromis spirulus niger*), *Cyprinus carpio* (Common carp) and *Clarias gariepinus (*African catfish).

Most of the fish caught is sold in Nairobi and the neighboring local markets such as Ekalakala, Mananja, Tumutumu, Karaba, Makutano, Masinga and Matuu town. Also, the fish are sold at Sagana bridge (Kwa Samaki) along Nairobi – Sagana road. Despite this fisheries potential, there is paucity of information on heavy metal contaminant levels in the Masinga reservoir and consequently limited understanding of the human health risks associated with consumption of fish from the reservoir.

1.3 Research Questions

To achieve the set objectives this study sought to answer the following research questions:-

1. What are the levels of physical parameters (pH, electrical conductivity, dissolved oxygen, temperature and turbidity) of water in Masinga reservoir?

2. What are the concentrations of heavy metals (lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu), chromium (Cr) and manganese (Mn) in surface water, sediments and in three selected fish species, *Oreochromis spirulus niger*, *Cyprinus carpio* and *Clarius gariepinus*?
3. Is there a relationship between the levels of heavy metals in surface water, sediments and in the muscle tissues of the three selected fish species?
4. Do the heavy metal concentrations in surface water, sediments and the three selected fish species exceed the WHO set limits?

1.4 Objectives

1.4.1 Broad Objective

The purpose of this study was to assess the extent of heavy metal pollution in surface water, sediments and selected fish species in Masinga reservoir.

1.4.2 Specific Objectives

This research project sought to achieve the following specific objectives

1. To find out the levels of physical parameters (pH, electrical conductivity, dissolved oxygen, temperature and turbidity) of water in Masinga reservoir.
2. To determine the concentration levels of heavy metals (lead, cadmium, zinc, copper, chromium and manganese) in surface water and sediments in Masinga reservoir.
3. To determine the concentration levels of heavy metal pollutants (lead, cadmium, zinc, copper, chromium and manganese) in three selected fish

species, Tilapia *Oreochromis spirulus niger*, Common carp *cyprinus carpio* and African catfish *Clarius gariepinus* in Masinga reservoir.

4. To find out whether there is a relationship between levels of heavy metals in surface water, sediments and the three selected fish species.

1.5 Research Hypotheses

1. There is no significant difference in the concentrations of heavy metals (Pb, Cd, Zn, Cu, Cr and Mn) in surface water, sediments and the selected fish species in Masinga reservoir.
2. There is no significant relationship between level of heavy metals (Pb, Cd, Zn, Cu, Cr and Mn) in surface water, sediments and in the selected fish species in Masinga reservoir.
3. The levels of heavy metal contaminants in water and selected food fish species do not exceed the WHO set limits for drinking water and food for human consumption.
4. The heavy metal concentrations in sediments do not exceed the WHO set limits for survival of aquatic organisms.

1.6 Significance of the Study

The increase of human population has amplified the need for food supply while the need for fish protein has increased the demand for fish and fish products. The global consumption of fish and derived fish products has generally increased during recent decades (Wim *et al.*, 2007). It has been predicted that fish consumption in

developing countries will increase by 57 percent, from 62.7 million metric tons in 1997 to 98.6 million in 2020 (Delgado *et al*., 2003). However, the levels of contaminants in fish and poor management of fisheries are of particular interest because of the potential risk to humans who consume them. Therefore, information gathered in this study is a contribution to understanding of heavy metal contamination in water, sediments and fish from Masinga reservoir. It is an assessment of the impact of anthropogenic activities in the catchment to the aquatic ecoystem. This information is important for decision making on sustainable development within Masinga reservoir catchment. This will enable effective monitoring of both environmental quality and the health of aquatic organisms in the reservoir. Finally, information gathered is a contribution to literature for other scholars with interests in heavy metal pollution research.

CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction

Aquatic ecosystems such as rivers, dams and lakes provide livelihood for rural populations in many developing countries in Africa. However, in the recent past, they have been subjected to various forms of degradation due to pollution arising from domestic wastes, industrial effluent, agricultural run offs and bad fishing practices (Ndimele, 2008). According to Bakare *et al.,* (2003) industrialization and human activities have partially or totally turned the environment into dumping sites for waste materials. As a result, many water resources have been rendered polluted and hazardous to man and other living systems.

Stable metals or metalloids whose density is greater than 4.5g cm^{-3} are termed as heavy metals and include lead, cadmium, mercury, iron, copper, zinc, nickel and manganese (Anderson, 2003). Metals are an integral component of the environment and living matter (Carolyn *et al.,* 2004, Nicholas *et at*., 1998). Some of them are essential elements without which, the biochemical processes in living organisms would collapse but when they exceed the normal concentrations, they become detrimental to the organisms. Heavy metal contamination particularly the non-essential elements may have distressing effects on the ecological balance of the recipient aquatic environment with a diversity of organisms. This has particular significance in ecotoxicology, since the heavy metals are highly persistent and have the potential to bio accumulate and bio magnify in food chain,

and become toxic to living organisms at higher trophic levels in nature. Heavy metal contaminations in inland waters can be monitored by using the metal levels in water; sediments and resident biota especially fish (Senarathne and Pathiratne, 2007).

According to Anim-Gyampo *et al.,* (2013), heavy metals tend to accumulate in soils and sediments after weathering processes and can be deposited in water bodies due to surface run-offs. Once the heavy metals come into the aquatic environment, they scatter in various components such as water, suspended solids, sediments and biota. The heavy metals of most environmental concern in water are lead (Pb), chromium (Cr), arsenic (As), cadmium (Cd), copper (Cu) and zinc (Zn) (Martin and Coughtrey, 1982). Contamination by these heavy metals can be expressed by their high concentrations in water, as well as in sediments and aquatic organisms (Pham *et al*., 2007). Cadmium, copper, lead and zinc salts are usually found in agricultural and industrial liquid wastes (Qiao *et al*., 2007) which are discharged into water resources. The metals accumulate from water to higher levels in fish tissues (Watanabe and Tanabe 2003; Sankar *et al*., 2006). The concentration of metals in water correlates positively with concentrations in fish tissue (Castro-Gonzalex *et al*., 2008).

2.2 Heavy Metal Contamination in Sediments

Contamination of sediments by heavy metals and other pollutants is considered by many regulatory agencies to be one of the major threats to aquatic ecosystems.

The importance of sediments as a sink for a range of substances including nutrients, hydrocarbons, pesticides and heavy metals has been highlighted in many past studies (Baldwin and Howitt, 2007). Sediments are one of the possible media in monitoring the health of aquatic ecosystems. They are ecologically important components of the aquatic habitat and play a significant role in maintaining the trophic status of any water body (Singh *et al*., 1997. Abraha *et al*., (2012) observed that sediments play a significant role in remobilization of contaminants in aquatic systems under favourable conditions and interactions between water and sediments. Like soils in the terrestrial system, sediments are the primary sink for heavy metals in the aquatic environment. Akan *et al*., (2010) observed that sediments in rivers do not only play important roles at influencing the pollution, they also record the history of their pollution.

Heavy metals once adsorbed on the sediments are not freely available for aquatic organisms. Under changing environmental conditions (temperature, pH, redox potential, salinity) of the overlying water these toxic metals are released back to the aqueous phase (Soares *et al*., 1999). The occurrences of enhanced concentrations of heavy metals especially in sediments may also be an indication of human-induced perturbations rather than natural enrichment through geological weathering (Binning and Baird, 2001; Eja *et al*., 2003). Heavy metal distribution and bioavailability in both sediments and the overlying water column have to be considered to obtain a better understanding of interactions between the organisms and their environment. Hence, the assessment of sediment is significant to study

the risk of aquatic ecosystem. Apart from water, sediments are also responsible of nutrients and pollutant transportation in aquatic environment.

Sediments capture hydrophobic chemical pollutants that enter water bodies (McCready *et al*., 2006) and slowly release the contaminant back into the water column (Chapman and Chapman 1996; McCready *et al*., 2006). Therefore, ensuring a good sediment quality is crucial to maintain a healthy aquatic ecosystem, which ensures good protection of human health and aquatic life. In addition to the physical and chemical relationships between sediments and contaminants, sediments are of fundamental importance to benthic communities in terms of providing suitable habitats for essential biological processes. Therefore, sediments provide an essential link between chemical and biological processes.

Sediments near urban areas commonly contain high levels of contaminants (Lamberson *et al*., 1992; Cook and Wells, 1996). This constitutes a major environmental problem faced by many anthropogenically impacted aquatic environments (Magalhaes *et al*., 2007). Sediments act as both carrier and sources of contaminants in aquatic environment (Shuhaimi, 2008). The contamination of sediments with heavy metals leads to serious environmental problem (Loizidou *et al*., 1992). Heavy metals may adsorb onto sediments or be accumulated by the benthic organisms; their bioavailability and toxicity depend upon the various forms and amount bound to the sediment matrices (Chukwujindu *et al*., 2007). Additionally, pollutants released to surface water from industrial and municipal

discharges, atmospheric deposition and run off from agricultural, urban and mining areas accumulate to harmful levels in sediments (Chukwujindu *et al*., 2007).

2.3 Heavy Metals in Fish

Fish enjoys a good reputation as a nutritious and healthy food. They are essential food items that provide high quality protein, vitamins, minerals and omega-3 fatty acids which have been associated with health benefits due to their cardio-protective effects (Wim *et al*., 2007; Gamal and Shamery, 2010). Despite the many health benefits associated with fish in a diet, there are also some health risks related to fish consumption, mainly due to potential adverse effects of heavy metal contamination. Jarup (2003) noted that heavy metals are well known environmental pollutants that cause serious health hazards to human beings; their effects are not immediate and show up after many years. These environmental pollutants represent a major problem in both developed and undeveloped countries of the world.

Aquatic biota has been used to monitor heavy metal pollution in aquatic ecosystems for decades (Etesin and Benson, 2007; Kamaruzzaman *et al*., 2011a). The choice of biota depends on several factors like heavy metal accumulating potential of the organism, motility, economic value among others (Ndimele and Kumolu-Johnson 2012). However, fish are the often preferred biota because of their big size which makes them easily indefinable and their ability to accumulate

heavy metals (Ghosh *et al*., 2006; Ndimele *et al*., 2011a). Also, fish is a bio-indicator because it is easy to be obtained in large quantity, potential to accumulate metals, long lifespan, easy to be sample and optimum size for analysis (Anim-Gyampo *et al*., 2013).

Therefore, fish are useful as sentinel species and biomonitors of metal pollution because they can help understand the risk to the aquatic ecosystem and to humans (Peakall and Burger, 2003). The use of wild and cultured food fishes as biomonitors of metal pollution in aquatic ecosystems is becoming popular throughout the world (Norrgren *et al*., 2000; Mansour and Sidky, 2002; Bervoets and Blust, 2003; Marcovecchio, 2004; Begum *et al*., 2005; Demirack *et al*., 2005; Storelli *et al*., 2006; Agarwal *et al*., 2007; Ploetz *et al*., 2007; Indrajith *et al*., 2008).

Heavy metals are non-biodegradable and they persist in the environment and may become concentrated up the food chain (Eja *et al*., 2003). This may lead to enhanced levels in tissues of fish (Eja *et al*., 2003) and other aquatic biota (Ramos *et al*., 1999). The region of accumulation of heavy metals within fish varies with route of uptake, type of heavy metal and species of fish concerned. The accumulation of contaminant residues may ultimately reach concentrations hundreds or thousands of times above those measured in the water, sediment and food (Goodwin *et al*., 2003 and Osman *et al*., 2007). For this reason, monitoring fish tissue contamination serves an important function as an early warning

indicator of sediment contamination or related water quality problems (Mansour and Sidky 2002; Barak and Mason 1990). Monitoring fish tissue contamination also enables detection of toxic chemicals in fish that may be harmful to consumers, and take appropriate action to protect public health and the environment.

Multiple factors including season, physical and chemical properties of water can play a significant role in metal accumulation in different fish tissues (Hayat *et al*., 2007). It is therefore of great significance to evaluate pollution effects on fish for both environmental protection and socio-economic reasons. A combination of biological monitoring (bioaccumulation) and measurements of water and sediment quality can provide a good indication of conditions and potential risks to a water body (Alaa and Osmanl, 2010).

Accumulation of metals in different fish species depends on their feeding habits, ecological needs, metabolism, age and size of fish (Peakall and Burger, 2003; Marcovecchio, 2004). Heavy metals accumulate in many important organs (Golovanova, 2008). Evidently heavy metals accumulate frequently in fish flesh and in internal organs (Dural *et al*., 2007). Supporting structures and gills mostly accumulate waterborne heavy metals, while stomach and intestines accumulate food-associated elements. The highest concentrations of heavy metals are found in fish liver, kidney and gills (Golovanova, 2008). Diet is the main route of exposure to heavy metals in the case of population not exposed to them. Thus, heavy metals

acquired through the food chain as a result of pollution are potential chemical hazards, threatening consumers. The consequence of heavy metal pollution can be hazardous to man through his food. Therefore, it is important to assess and monitor heavy metal in aquatic environments (water, sediment and biota).

2.4 Effects of Heavy Metals to Aquatic Organisms and Man

Despite progress made in environmental waste management, heavy metals still pose immense health hazards to human and aquatic biota. Unlike other classes of pollutants which can be biodegraded and totally destroyed, heavy metals are non biodegradable (Wepener *et al*., 2001), and can neither be created nor destroyed. However, heavy metals might be altered from more toxic form or complexes to more stable and less toxic compounds (Viljoen, 1999).

Discharge of heavy metals into a river or any aquatic environment can change both aquatic species diversity and ecosystems, due to their toxicity and accumulative behavior (Heath, 1987; Allan, 1995). Aquatic organisms such as fish and shell fish accumulate metals to concentrations many times higher than present in water or sediment (Olaifa *et al*., 2004, Gumgum *et al*., 1994). They can take up metals concentrated at different levels in their different body organs (Khaled, 2004).

In an aquatic environment, toxicity can be influenced by various abiotic environmental factors such as oxygen, calcium/water hardness (Chillebaert *et al.*, 1995) pH, and temperature (Kotze *et al.*, 1999). Temperature especially is an

important factor affecting metal toxicity, since most aquatic organisms are poikilothermic (Hilmey *et al.,* 1987). Studies have shown that as water temperature rises, toxicants in water become more lethal to fish at lower concentrations (Van Der Merwe *et al.,* 1993).). Other factors that can play a role are organic matter (Chillebaert *et al.,* 1995), carbon dioxide, metabolic activities, biological half-life of the metal (Kargin and Cogen, 1999), suspended solids, total organic carbon (Cairns and Mount, 1990), interactions between pollutants and the developmental stages of the organisms, and intraspecific variations in susceptibility to metals. Studies carried out on fish have shown that heavy metals have toxic effects. They alter physiological activities and biochemical parameters both in tissue and in blood of fish (Larsson *et al*., 1985; Nemesok and Huphes, 1988; Abel and Papoutsouglou, 1986). Elements such as mercury, cadmium, copper and zinc are considered most dangerous in the ecotoxicological aspect (Golovanova, 2008).

Consumption of biota from contaminated aquatic bodies is an important route of exposure to pollutant compounds. However, water quality criteria for fish have not received the attention that they deserve. All too often, water has been considered quite adequate for fish as long as there is no obvious mortality ascribed to known pollutants.

2.5 Environmental Aspects of Heavy Metals

Heavy metals are of particular concern in the environment since they exhibit both toxicity and persistence and are known to bioaccumulate in the food chains

(WHO, 2000). They also have deleterious effects on both plant and animal life, in addition to risk on human health (Kinyua and Pacini, 1991). Both the beneficial and toxic effect of metals is influenced by other elements in the environment and biological factors. Toxicity can often be lessened or even concentrated by biological adaptation. Studies have indicated that toxicity of metals such as cadmium and copper is primarily due to the presence of the free metal ion and thus may not be directly related to the total metal concentration (Shepherd, 1980).

2.5.1 Copper

Copper is an essential constituent of living systems (Rand and Petrocelli, 1988; Carolyn *et al.,* 2004; Nicholas *et al*., 1998)). It is one of the essential elements for human beings. It is widely distributed metal in nature. Copper can exist in aquatic environment in three forms namely soluble, colloidal and particulate. Excess of copper in human body is toxic and causes hypertension and produces pathological changes in brain tissues. Excessive ingestion of copper is responsible for specific disease of the bone (Krishnamurthy and Pushpa 1995). High doses may also cause anaemia, liver and kidney damage, stomach and intestinal irritation (Tirkey *et al*., 2012). Copper occurs in metalloproteins such as hemocyanin an oxygen carrier in molluscs and anthropods, cytochrome oxidases and plastocyanin (Hughes, 1975). Copper ions (Cu^{2+}) are toxic to most life forms, 0.5 ppm being lethal to many algae species (O'Dell and Campell, 1971). Copper is highly toxic to invertebrates and moderately so to mammals in trace amounts. Wandiga *and* Onyani (1989) reported the average copper concentrations in sediments in Lake Victoria as

83.3mg kg^{-1} while in Lake Nakuru it ranged between 2 - 3.67mg kg^{-1}. According to Oyaro *et al,* (1999) the copper mean concentration in soils in Nairobi is 40.27 μg g^{-1}. In general copper pollution sources include, mining activities and intensive use of copper pellets in pig farming.

2.5.2 Lead

Lead (Pd) in the environment arises from both natural and anthropogenic sources. It is a natural constituent of air, water and biosphere (Alala, 1981). Lead is an undesirable trace metal less abundantly found in earth's crust. Exposure can occur through drinking water, food, air, soil and dust from old paint containing Pb. Lead is a serious cumulative body poison. High levels of exposure may result in biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system (Tirkey *et al*., 2012).

Lead is a systemic agent affecting the brain (Tver, 1981). The toxicity of lead is based on the fact that it is a potent enzyme inhibitor because it binds sulphydryl (SH) groups. The pathological effects of lead are observed in three organs systems: the nervous system, kidney and haematopietic system. Lead accumulates in the bones and soft tissues, particularly in the brain, resulting in its reduced functioning (Omwenga, 2003, Rand and Petrocelli, 1988, Alala, 1981). In aquatic organisms, crustaceans are the most sensitive to Pb below gastropods, insect larvae and the single annelid species (Ingersoll and Winner, 1982). After longer

exposures, the gastropods at least become as sensitive as the crustaceans species. Lead is extensively used and is one of the most widespread metals in the environment largely due to human activities (Tarr and Miessler, 1999). The sources include burning of lead based petroleum fuels, organic and inorganic lead compounds now used in a variety of commercial products and industrial materials including plastics, storage batteries, bearing alloys, insecticides, ceramics, cable sheathings, sheeting, radiation shields and even some paints (Mutwiri, 2001).

2.5.3 Cadmium

It is non-essential element known to have a toxic potential. The concentration of cadmium in lithosphere is low. Cadmium is highly toxic and responsible for several cases of poisoning through food. Small quantities of cadmium cause adverse changes in the arteries of human kidney. It replaces zinc biochemically and causes high blood pressures and kidney damage. It interferes with enzymes and causes a painful disease called Itai-itai (Rajappa *et al*., 2010).

Cadmium even in low concentration is quite toxic to human health (Mohan *et al*., 1998). Cadmium can readily disrupt the normal functioning of plant enzymes because of its affinity for binding to sites containing sulphydryl grouping (Carolyn *et al.,* 2004, Nicholas *et al*., 1998). Due to its physicochemical similarity with zinc, an essential divalent ion, it can interfere with key metabolic processes by replacing zinc. Cadmium causes reduced plant growth and complete failure. Absorption of cadmium from the gastrointestinal tract is increased if there is a

deficiency in calcium and iron (National Research Council Canada, 1979). In contaminated water, dissolved Cd levels are mainly dependent upon pH (National Research Council Canada, 1979). High concentration of cadmium occurs at neutral and alkali pH.

The main sources of cadmium are industrial activities as the metal widely used in electroplating, pigments, plastic, stabilizes and battery industries. Cadmium is used industrially as an anti-friction agent, as a rust inhibitor, in plastic manufacturing, as an orange colouring agent in enamels and in paints and in alkaline batteries (Purves, 1977). Cadmium is also released in cadmium fungicides, cadmium-based enamel and cadmium pigments, in nickel-cadmium dry cell batteries and finds large-scale use as an impurity, like in zinc products, phosphates fertilizers and coal (Fulkerson *et al.*, 1973).

Cadmium derives its toxicological properties from its chemical similarity to Zn an essential micronutrient for plants, animals and humans. Cd is biopersistent and once absorbed by an organism, remains resident for many years (over decades for humans) although it is eventually excreted (Tirkey *et al*., 2012). High exposure leads to obstructive lung disease and can even cause lung cancer. Cadmium produce bone defects in humans and animals (Tirkey *et al*., 2012).

2.5.4 Zinc

Zinc is an essential element for the life of animal and human beings. It is found in virtually all food and potable water in the form of salts or organic complexes

(WHO, 2011). According to Momtaz (2002), the most common minerals of Zn are zinc sulphide (ZnS), zincite (ZnO), and smithsonite (ZnCO3). Zinc is used in many industries for example, in the manufacture of dry cell batteries and production of alloys such as brass or bronze (Momtaz, 2002). The main sources of Zn pollution in the environment are zinc fertilizers, sewage sludges, and mining (Bradi, 2005). Urban runoff, mine drainage, and municipal sewages are the more concentrated sources of zinc in water (Damodharan, 2013).

Zinc plays a vital role in the physiological and metabolic process of many organisms (Rajappa *et al*., 2010). It is an essential element in animal diet but it is regarded as potential hazard for both animal and human health (Amundsen *et al.,* 1997). It plays an important role in protein synthesis. Zinc shows fairly low concentration in surface water due to its restricted mobility from the place of rock weathering or from the natural sources (BIS, 1998).

Zinc may be toxic to aquatic organisms but the degree of toxicity varies greatly, depending on water quality characteristics as well as species being considered (Datar and Vashishtha, 1990). The permissible limit of zinc in water is 3 mg L^{-1} (WHO, 2008). Drinking water containing high levels of zinc can lead to stomach cramps, nausea and vomiting (Damodharan, 2013). Other clinical signs of Zn toxicity have been reported as diarrhea, bloody urine, liver failure, kidney failure and anemia (Duruibe *et al.,* 2007).

2.5.5 Chromium

Chromium is an essential micronutrient for animals and plants. It is considered as a relative biological and pollution significance element (Rajappa *et al*., 2010). Generally the natural content of chromium in drinking water is very low ranging 0.01 to 0.05 mg l^{-1} except for regions with substantial chromium deposits (Wedepohl, 1978).

Elevated concentration can result from industrial and mining processes (Datar and Vashishtha, 1990). Fish are usually more resistant to Cr than other aquatic organisms, but they can be affected sub-lethally when the concentration increases (Krishna *et al.*, 2014).

2. 5.6 Manganese

The element manganese (Mn) is present in over 100 common salts and mineral complexes that are widely distributed in rocks, in soils and on the floors of lakes and oceans (Damodharan, 2013). These Mn minerals include sulfides, oxides, carbonates, silicates, phosphates, arsenates, tungstates, and borates; however, the most important Mn mineral is the native black manganese oxide, pyrolusite (MnO_2). According to Bradi (2005) the other main ores are rhodochrosite ($MnCO_3$), manganite (Mn_2O_3-H_2O), hausmannite (Mn_3O_4), braunite ($3Mn_2O_3$-$MnSiO_3$), and rhodonite ($MnSiO_3$).

Manganese is used for production of ferromanganese steels, electrolytic manganese dioxide for use in batteries, alloys, catalysts, antiknock agents,

pigments, dryers, wood preservatives and coating welding rods (Bradi, 2005). It is also used as an oxidant for cleaning, bleaching and disinfection (as potassium permanganate) and as an ingredient in various products (WHO, 2011).

Manganese is an essential micronutrient present in all living organisms, as it functions as a co factor for many enzyme acticities (Suresh *et al.*, 1999). It is necessary for the formation of connective tissues and bone, growth, carbohydrate and lip metabolism, embryonic development of inner ear, and reproductive function (WHO, 2011 and DWAF, 1996). Mn is a metal with low toxicity but has a considerable biological significance and seems to accumulate in fish (Kumar *et al.*, 2011). According to Krishna *et al.,* (2014), high Mn concentration interfers with central nervous system of vertebrates, hence a matter of concern as the consumption of Mn contaminated fish could result to health risks to the consumers. High concentration of Mn causes liver cirrhosis and also produces a poisoning called Manganese or Parkinson disease (Bradi, 2005).

2.6 Fish Production in Kenya

The fisheries sector plays a significant role in employment and income generation in Kenya. The sector supports about 1.1 million people directly and indirectly, working as fishers, traders, processors, suppliers and merchants of fishing accessories and employees and their dependants (GOK 2012). In the year 2012, fish production from Inland, Aquaculture and Marine artisanal fisheries amounted to 154,015 metric tonnes with an ex-vessel and farm gate value of Kshs. 18 billion

(Figure 2.1). Inland capture fisheries contributed 80% of Kenya's total fish production, with the principal fishery being that of Lake Victoria (77%) and Lake Turkana (1.94%). Other freshwater-bodies of commercial importance include lakes Naivasha, Baringo, Jipe, the Tana River dams and the Tana River's delta.

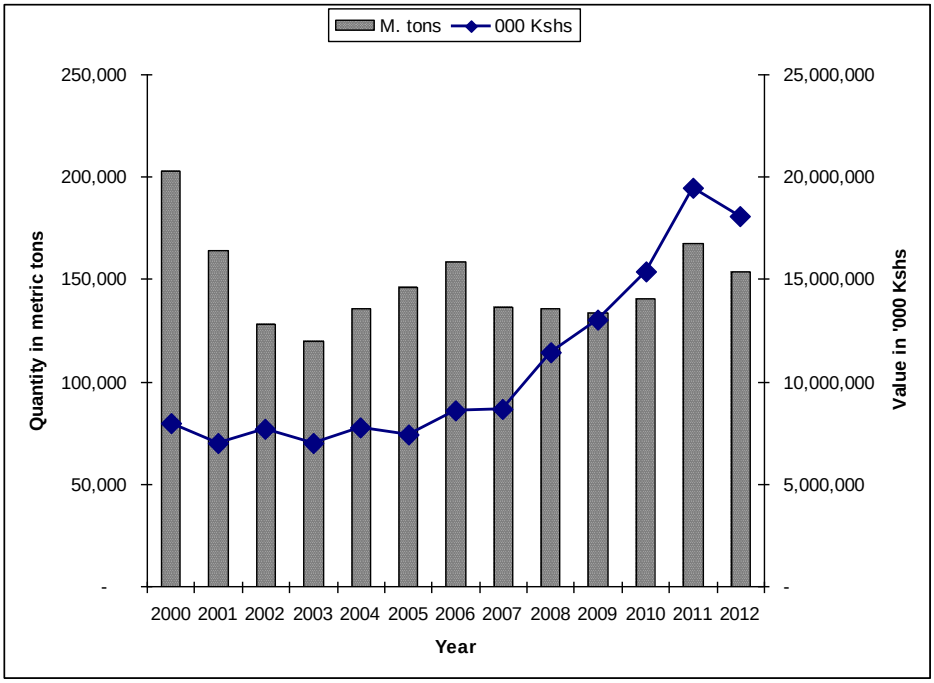

Figure 2.1: Fish production in Kenya by quantity and value 2000-2012 (GOK, 2012)

2.6.1 The Tana River Dams' Fishery

According to GOK (2012), the Tana River dams (Masinga, Kamburu and Kiambere) had fish catches totaling 967 metric tonnes with an ex-vessel value of Kshs 81,609,469 for the year 2012. This production reflected an increase of 32.1% in quantity and 51.7% in ex-vessel value compared to 2011 figures of 732 metric tonnes valued at Kshs 53,781,415 (Figure 2.2). The contribution of the landings by dams was as follows: Masinga dam 608 metric tonnes (63%),

Kiambere 290 metric tonnes (30%) and Kamburu 69 metric tonnes (7%) (GOK, 2012). Masinga dam has got four landings sites; namely Tututumu, Mananja, Riakanau and Ekalakala while Kamburu has only one gazetted landing site, which is Kisumu Ndogo. Kiambere dam has got two landing sites; these are Jua kali and Katooni/Korokocho.

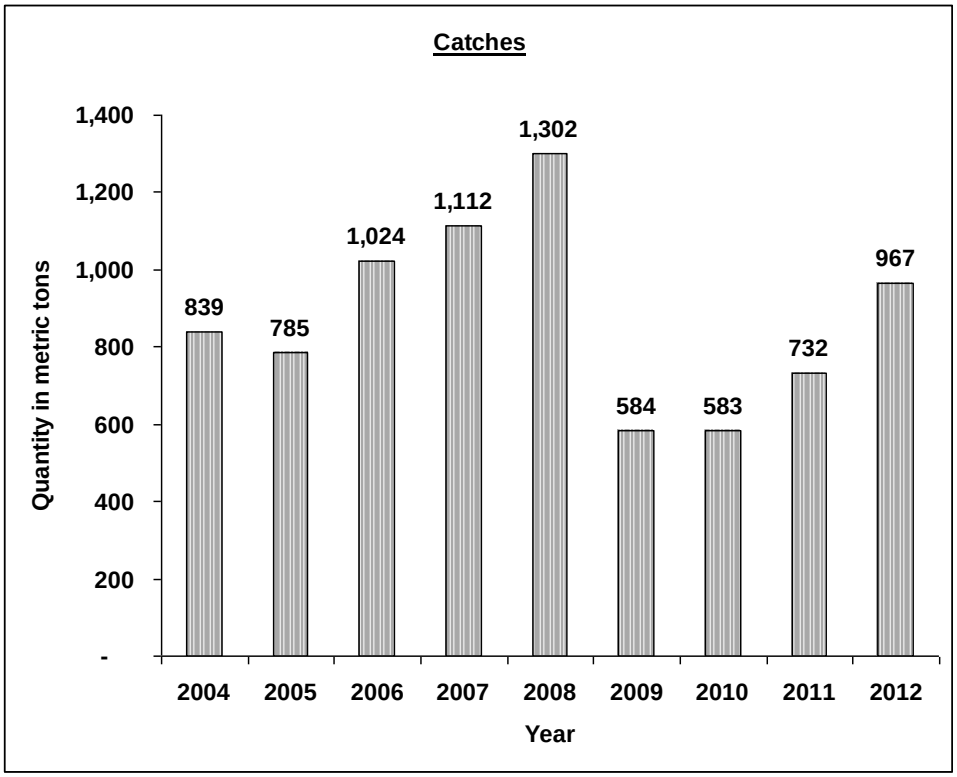

Figure 2.2: Tana River dams' fish catch trends in metric tonnes 2004 – 2012 (GOK, 2012)

In the 2012, fish catches landed at the gazetted sites were Ekalakala with 226 metric tonnes (23%) of the total dams' landings. This was followed by Jua kali 172 metric tonnes (18%), Mananja 152 metric tonnes (16%), Riakanau with 140 metric tonnes (14%), Katooni/Korokocho 118 metric tonnes (12%), and finally

Kisumu ndogo 69 metric tonnes or 7% of the total landings from the dams (GOK 2012). Fishing in all the dams is mainly passive using gillnets, traditional traps, and hand lines. Fishing effort in 2012 was 316 fishers using 180 fishing crafts and operating about 10,900 gillnets and 16,600 hooks and 560 traditional traps. The main market of the landed catches was sold in Nairobi mainly Gikomba market.

The most important species in the catches were *Tilapia spp,* Common carp (*Cyprinus carpio*) and African catfish (*Clarias gariepinus*). Landings of tilapia species were the highest at 463 metric tonnes (or 47.8%) followed by *Cyprinus carpio* 295 metric tonnes (30.5%), *Clarias gariepinus* 207 metric tonnes (21.5%) and the *Eels* with only one metric ton. The rest of the species namely *Barbus spp, Labeo spp* and *Mormyrus* had their catches below 100 Kgs. Tana River dam's fish production is determined by the level of water in the dams and this causes fluctuations of the total annual landing depending on the water level in the dams.

2.7 The Main Fish Species in Masinga Reservoir

2.7.1 Common Carp (*Cyprinus carpio*)

Common carp *Cyprinus carpio* is native to Asia and Eastern Europe; however it has been introduced into freshwater environments worldwide. It is considered as an invasive species (Yousafzai *et al*., 2012). *Cypinus carpio* prefers large bodies of slow or standing water and soft vegetative sediments. Common carps are omnivorous. Their temperature tolerance range is 1.6 – 30^0C. Common carp can eat a vegetarian diet of water plants, but prefers to scavenge the bottom for

insects, crustaceans including zooplankton and benthic worms (Yousafzai *et al*., 2012).

Due to their high fecundity and their feeding habit of grubbing through bottom sediments for food they are notorious for altering their environment. By feeding, they may destroy, uproot and disturb submerged vegetation causing serious damage to other fish populations. According to Narayan and Vinodhini (2008), Common carps are highly resistant to aquatic pollution. Common carp can grow to a maximum length (1.5m) and weight (37.3kgs). The largest recorded carp was caught by an angler in 2007 at Rainbow Lake near Bordeaux, France and weighed 40.1kgs (Yousafzai *et al.*, (2012).

2.7.2 African catfish (*Clarias gariepinus*)

Catfishes are a large group of predominantly freshwater fishes that are widely distributed throughout the world. They reach their greatest diversity in the continents spanning the equator–South America, Africa and Asia, and are a dominant group in the largest rivers such as the Amazon and the Zaire (Bruton, 1988). *C. gariepinus* has the widest latitudinal range in the world (about 70^0 latitude) (Bruton, 1988).

This species inhabits a very wide range of inland waters, including streams, rivers, pans, swamps, underground sinkholes, shallow and deep lakes as well as impoundments. *C. gariepinus* has a wide mouth, which gives it the ability to feed on a variety of food items, ranging from minute zooplankton to fish. Babiker

(1984) reported *C. gariepinus* to be omnivorous. Bruton (1988) found out that in Lake Sibaya in Zululand, juveniles of up to 50-mm total length (TL) fed mainly on chironomid larvae, shrimps and small planktonic or benthic crustaceans. According to Bruton (1988) food recorded from catfish stomachs also included frogs, snakes, fledging birds and small mammals as well as algae, macrophytes, seeds and fruits.

2.7.3 Tilapia (*Oreochromis spirulus niger*)

This is an endemic ciclid of the Tana and Athi River basins (Okeyo, 1998). Jumbe (2003), reported a decline in the mean size of this tilapiine in Masinga reservoir due to extensive use of small mesh sized gill nets by fisher folk. The growth rate of *O. spirulus niger* has been reported as to be moderate and comparable to other *Oreochromis* species in natural lakes (Njiru and Ojuok, 1997; Rabuor *et al.,* 1998).

CHAPTER THREE: MATERIALS AND METHODS

3.1 Introduction

This chapter introduces the study area, data collection procedures in the field, sample collection and processing. The method used to determine heavy metals in water, sediments and fish is also discussed.

3.2 Study Area

3.2.1 Study Area Location

The study was carried out in Masinga reservoir which is located 100 km North East of Nairobi. It lies between latitude (0^0 45′S; 1^0 11′ S) and longitude (37^0 0′ E; 37^0 46′E) with an altitude of 1056.5 m above sea level. It is the upper most cascade dam of the seven forks development scheme on the Tana River. The dam was constructed between 1976 and 1980 as a storage reservoir to regulate water flows to the lower dams whose water levels fluctuated drastically during the dry season. It is a multi-branched type with a large number of shallow bays and has a high shore line surface area ratio.

The reservoir has a full operation surface area of 125km^2 and extends 45km upstream along the Tana River (Figure 3.1). The mean depth is 13.8 m while the maximum depth at the dam wall is 48 m (Jumbe, 2003). The reservoir provides hydro-electricity power (40mw), irrigation water for agriculture and commercial fishing.

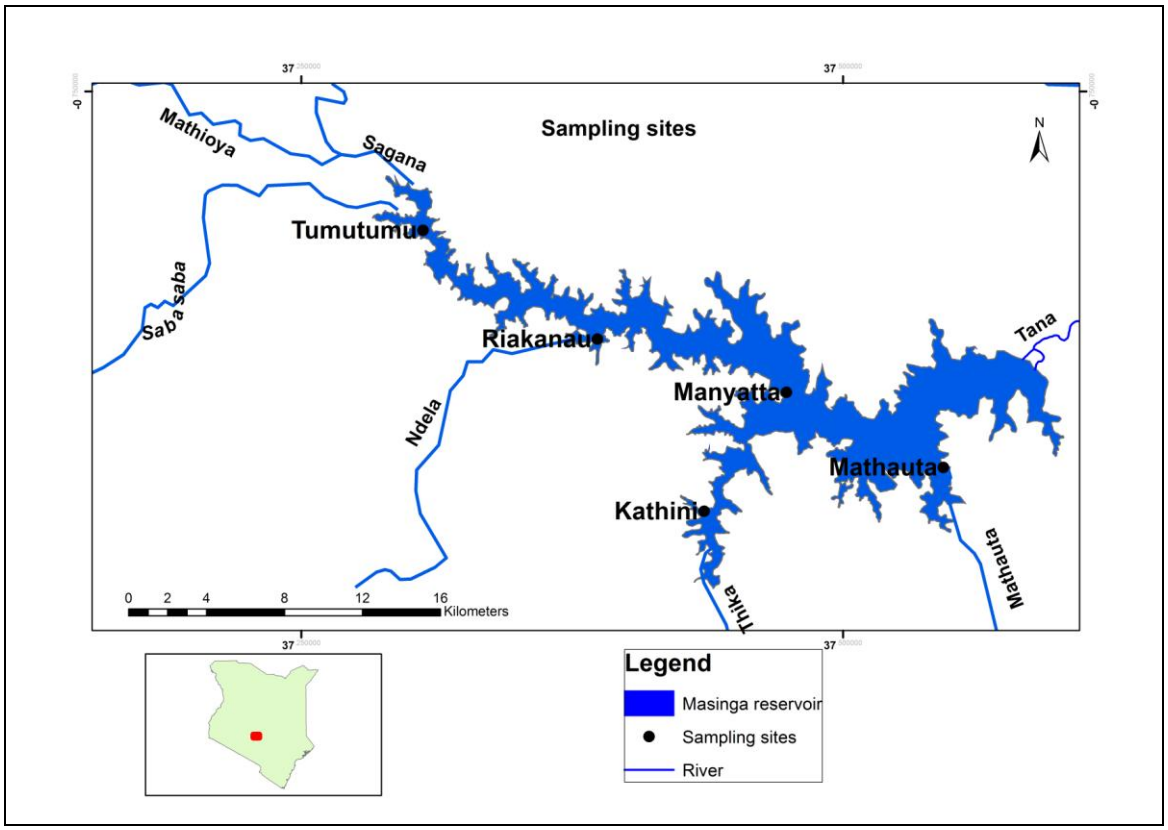

Figure 3.1 Map showing the location of Masinga reservoir and sampling sites

3.2.2 Climate

The climate of the Masinga basin is influenced by altitude and latitude. It is characterized by a bimodal distribution of rainfall with long rainy season occuring from March to May and the short rainy season in October and to December (Agwata, 2005). Close to the dam rainfall is scarce and erratic. Relative humidity ranges between 50 – 80% and evaporation rates are high (Knight and Piesold, 1997). Minimum temperatures range from 21^0C in July and August to 24^0C in October while maximum temperature ranges from 25.5^0C to 31^0C.

The vegetation of the area surrounding Masinga dam is described as natural overgrazed *Acacia/Commiphora* bushed grasslands (Atkin, 1984). The upper most catchment area (2500 – 4000 m above sea level) is forested and receives an annual rainfall of over 2000mm. The adjacent areas are tea zones (1500 – 2500 m above sea level) and they receive rainfall ranging between 1400 – 1600 mm and intensely farmed. Below the tea zone are the upper and lower coffee zones (1200 – 1500 m above sea level) which receive rainfall ranging 1200 – 1400 mm per year. The areas adjacent to the reservoir are dry and receive less than 800 mm of rainfall (Atkin, 1984).

3.2.3 Drainage

The Tana River is the longest river system in Kenya (approximately 1, 200 km) with a catchment area of about 120, 000 km^2 and an average annual discharge of 4 x $10^9 m^3$ (Kitheka *et al*., 2005). The Tana River and Thika River sub basins form the Masinga dam catchment area and drain into Masinga reservoir. The Thika sub basin is drained by Chania, Kimakia, and Thika river systems, with the later draining into Masinga reservoir. The Tana sub basin is drained by several perennial rivers. These include Saba Saba, Maragua, Mathioya, and Sagana (Figure 3.1). In addition there are numerous seasonal streams which drain into the reservoir. Masinga dam has a catchment area of 7,355km^2 and creates the largest storage and regulatory structure on the Tana River for regulating flows for downstream hydropower dams. The catchment lies East of Aberdares ranges and South of Mount Kenya in a rich agricultural area.

3.2.4 Economic Activities in the Area

The Masinga catchment is a high potential area characterized by horticultural and floriculture farming, large scale coffee and tea plantations. In Thika sub basin there are manufacturing factories within Thika town area. There is also subsistence farming around the plantation farms. The livelihoods of the total population within the catchment to a large extent depend on the environmental health in the Tana River and its tributaries remaining in good condition (UN-WATER, 2006).

3.3 Selection of Study Area

Masinga reservoir is located in a catchment basin with intense human activities. According to UNEP (2000), economic activities in the catchments would affect the status of aquatic ecosystems. The Upper Tana Catchment basin is characterized by catchment degradation (deforestation and encroachment), poor farming methods leading to soil erosion and siltation into water bodies and farming along river bank reserves. The key environmental issues include catchment degradation due to pollution from agro-based industries, agro-chemicals, urban effluent, car washing, soil erosion (siltation), river bank encroachment and industrial discharge (UN – WATER, 2006).

All these human activities within the catchment lead to anthropogenic pollutants being transported in the streams, rivers and other municipal drainage water systems; either dissolved in the water or attached to suspended matter and

eventually gets into the Tana River dams. Over 90% of Upper Tana Catchment drains into Masinga dam which is along the Tana River system. Therefore, the dam was chosen for this study because the impacts caused by human activities in the catchment are transmitted to receiving waters of Masinga reservoir. Also, most of the fish obtained from the Tana River dams are from Masinga dam. The reservoir is a source of livelihood to many fisherfolk and fish traders who live near the dam.

3. 4 Sampling

During a field reconnaissance (August 2012), five sampling sites were identified from the Masinga reservoir (Figure 3.1). The dam was divided into three regions; the upper, middle and lower regions. The upper and middle regions had two sites each (Tumutumu, Riakanau, Manyatta and Kathini respectively), while the lower region had one site (Mathauta). The five sampling sites were chosen to represent different sub basins that drain into the reservoir in order to understandard the influence of natural and human activities on the reservoir (Figure 3.1). The geographical location of each selected sampling site within the reservoir is shown in Table 3.1. Sampling was carried out once a month for one year (January 2013 – December 2013) in all the sampling sites in reservoir

3.4.1 Sampling and Storage of Water

Water sampling was done according to the procedure described by Ndimele and Kumolu-Johnson (2012). Water samples from all five (5) sampling sites were

collected at a depth of about 0.3m below water surface into 500 ml plastic bottles. Prior to sampling, the bottles were cleaned with 10% nitric acid and rinsed with distilled water. The bottles were rinsed three times with the dam water at the time of sampling. Samples were then collected by direct immersion of the sampling bottle into the dam. Immediately after sample collection, 2 ml nitric acid (AR grade) was added to the water samples to reduce adsorption of metals onto the walls of the plastic bottles. Sample bottles were then labeled to indicate date of sampling and the sampling site. Samples were transported in an ice-box to the laboratory and stored at 4^0C awaiting analysis.

Table 3.1 Geographical coordinates and water depth of sampling sites in Masinga Reservoir

Sampling Site	**Latitude**	**Longitude**	**Depth (m)**
Kathini (S1)	00^0 94′ 322″ S	037^0 43′ 237″ E	10.33 ± 0.99
Mathauta (S2)	00^0 92′ 571″ S	037^0 54′ 548″ E	22.42 ± 2.50
Manyatta (S3)	00^0 88′ 736″ S	037^0 47′ 279″ E	21.00 ± 6.70
Riakanau (S4)	00^0 86′ 476″ S	037^0 38′ 770″ E	7.25 ± 1.14
Tumutumu (S5)	00^0 81′ 416″ S	037^0 30′ 621″ E	7.58 ± 2.02

3.4.2 Sampling and Storage of Surface Sediments

Sediment samples were taken from the bottom surface (1-2 cm thick) using an Eckman grab according to Osman and Kloas (2010). For each sample, three sediments grabs were randomly taken, homogenized and kept in clean polyethylene bags. The polythene bags were then labeled to indicate sampling station and date of sampling. Samples were then stored in ice box for transportation to the laboratory. In the laboratory, the samples were kept in a freezer at -20^0C until they were processed for heavy metal analysis.

3.4.3 Sampling and Storage of Fish

Tilapia *Oreochromis spirulus niger* and Common carp *Cyprinus carpio*, were caught from all five sampling sites using gill nets (Plate 3.1). A total of 157 Tilapia and 165 Common Carp fish samples were caught during the study period. A total of 164 African catfish *Clarias garipeinus* samples were obtained from all five sampling sites by use of hook and long lines that had been cast and left overnight (Plate 3.2). Fish samples obtained were immediately kept in pre-cleaned polythene bags, sealed, labeled and kept in ice boxes for transportation to the laboratory at Kenyatta University. In the laboratory, total length (cm) and weight (grams) were recorded. The samples were then kept in a deeper freezer until muscle tissues were extracted for analysis.

Plate 3.1: Tilapia and Common carp fish samples respectively caught using gill nets in Masinga reservoir

Plate 3.2: African catfish sample caught using hook and long line in Masinga Reservoir

3.5 Field Measurements

The physical parameters were measured in the field at the time of collecting samples between 7 am and 11am.

3.5.1 Water Temperature

Surface water temperature was determined on site using temperature sensor of a dissolved oxygen probe (Model: DO 5510 M.R.C). The probe was immersed in

the reservoir water to a depth of 0.3 m and allowed to stabilize before temperature readings were taken in ^{0}C.

3.5.2 pH

The pH of the water was measured on site using a portable pH meter (Model: HI 8314 HANNA instruments, Romania). The pH probe was lowered to a depth of about 0.3 m allowed to stabilize and pH value was read.

3.5.3 Dissolved Oxygen

Dissolved oxygen (DO) was measured on site using Oxygen meter (Model: DO - 5510 M.R.C). The DO probe was immersed into the reservoir water a depth of 0.3 m. While gently stirring the water with the DO probe, the readings were allowed to stabilize and DO read in mg L^{-1}.

3.5.4 Electrical Conductivity

A multi-range conductivity meter (Model: HI 9033 HANNA instruments, Romania) was used to measure electrical conductivity (EC) of surface water in all sampling sites. The meter was lowered into the reservoir water to a depth of 0.3 m then allowed to stabilize before taking the conductivity readings in µS cm^{-1}.

3.5.5 Turbidity

The turbidity of water in all sampling sites was determined by use of a turbidity meter (Model: 2100P, Hach Company, USA). The measurements were read in Nephelometric Turbidity Units (NTU).

3.6 Laboratory Analysis

3.6.1 Stock and Working Standard Solutions

Stock standard solutions containing 1000 mg L^{-1} of Cu, Zn, Cd, Pb, Cr and Mn were prepared from metal salts (Analytical Grade) using nitric acid. Working standards for all the metals were prepared from the stock solutions by serial dilutions in distilled water.

3.6.2 Calibration of Instrument

To determine the instrument signal response to changes in concentration, calibration was done using working standard solutions of known and increasing concentrations for each analyte element of interest. By measuring the signals of the working standards, the AAS constructs a suitable calibration curve of response /absorbance verses concentration. The AAS uses this suitable graph to determine concentrations of unkown analyte. In this study the actual concentration of each heavy metal in the samples was calculated using the formula:

$$\text{Actual concentration } (\text{mg kg}^{-1}) = \frac{\text{Digested concentration } (\text{mg L}^{-1}) \times \text{Volume digested (L)}}{\text{Weight of dried sample (kg)}}$$

3.6.3 Digestion of Water Samples for Metal Analysis

Digestion of the water samples were done in triplicates using concentrated nitric acid (Analytical Grade) according to method described by Zhang (2007). Concentrated acid (5 ml) was added to 50 ml of sample water in a 100 ml beaker, and then heated on a hot plate to boil until its volume reduced to 20 ml. Another 5

ml of concentrated HNO_3 was added and then heated for 10 minutes and allowed to cool.

About 5 ml of nitric acid was used to rinse the sides of the beaker and the solution filtered using Whatman 0.42µm filter paper into a 50 ml volumetric flask and topped up to the mark with distilled water. A blank solution was similarly prepared. Heavy metal analysis was done using Varian Atomic Absorption Spectrometer (model Spectra AA-10) at the Mines and Geological Department, Nairobi. The blanks were aspirated along with the analytical samples in order to correct background adsorption. The operating conditions of the instrument (AAS) were set according to manufacturer's specifications (Table 3.2).

3.6.4 Processing and Digestion of Sediments for Metal Analysis

Each sediment sample was thawed at room temperature (25^0C – 28^0C) and put into pre-acid cleaned evaporating beakers. The sediments were then dried at temperature of 50^0C in an oven until a constant weight was obtained. The dried sediment samples were ground using a porcelain mortar and pestle and sieved through a 2 mm mesh plastic sieve.

For each sediment sample, 2 g was weighed using Shimadzu electronic weighing balance (Model ATX 224) into 100 ml acid cleaned beakers. Digestion was done using concentrated nitric acid (Analytical grade) and hydrogen peroxide. All the digested samples were filtered using Whatman 0.42µm filter paper into a 50 ml volumetric flask and topped up to the mark with distilled water (Plate 3.3). The

filtrate was analyzed for heavy metal analysis using AAS. A blank solution was similarly prepared. The AAS working conditions were set as shown in Table 3.2.

Table 3.2: Instrument (AAS) operating conditions

Element	**Cu**	**Zn**	**Cd**	**Pd**	**Cr**	**Mn**
Lamp current (mA)	3	3	5	8	7	5
Fuel	Acetylene	Acetylene	Acetylene	Acetylene	Acetylene	Acetylene
Support/Oxidant	Air	Air	Air	Air	Nitrous oxide	Air
Wave length (nm)	324.7	213.9	228.8	217.0	357.9	279.5
Slit width (nm)	0.5	1.0	0.5	1.0	0.2	0.2
Detection limit (mg L^{-1})	0.003	0.002	0.006	0.02	0.005	0.003

Plate 3.3: Filtering of digested sediments at Environmental Sciences laboratory, Kenyatta university.

3.6.5 Processing and Digestion of Fish Tissues for Metal Analysis

The deep frozen fish samples for the three fish species (*Oreochromis spirulus niger*, *Cyprinus carpio* and *Clarias gariepinus*) were thawed at ambient laboratory temperature overnight. The skin of each fish sample was removed using plastic knives to avoid metal contamination and this was followed by extraction of fish muscles. Fish muscles were put in a pre-acid washed and oven-dried crucibles. The samples were then dried to a constant weight in an oven at 50^0C (Plate 3.4). The dried fish samples were allowed to cool in a desiccator at room temperature.

After cooling, 2 gm of fish muscles was accurately weighed using a Shimadzu electronic weighing balance (Model ATX224) and transferred into a clean a beaker. Dried fish samples for each fish species were digested in triplicates according to method described in APHA (2005). To each weighed fish muscle, 18 ml of concentrated nitric acid was added and heated at 100 ^{0}C on a hot plate in a fume hood chamber. A few drops of hydrogen peroxide (analytical grade) were added until there were no brown fumes.

The digested fish samples solution was each filtered using Whatman 0.42µm filter paper in a 25 ml volumetric flask and topped to the mark with distilled water. The filtrate were each put into 60 mls pre – acid cleaned plastic bottles (Plate 3.4) and metal analysis done using a computerized Varian Atomic Absorption Spectrophotometer (model Spectra AA-10) at Mines and Geological department

under working conditions as shown in Table 3.2. Blank solutions were prepared in similar manner as for the samples.

Plate 3.4: Drying of extracted fish muscles and digested fish samples in bottles at the laboratory

3.7 Statistical Data Analysis

Data analysis was done using a computerized statistical programme (STATISTICA 8.0, 2007). The data were subjected to one way analysis of variance (ANOVA) and significant differences accepted at $p \leq 0.05$ (Zar, 2001).

Where significant differences were found, the mean values were separated using post-hoc Tukey's (HSD) test. Correlation analysis was done to determine associations among various variables. Descriptive statistics for all collected data were also obtained using STATISTICA software.

CHAPATER FOUR: RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter presents the findings of physical parameters and heavy metal concentrations in sediments, surface water and three selected food fish species (Tilapia, Common Carp and African catfish). Discussions of results and comparison with other similar studies are also given in this chapter.

4.2 Physical Parameters

4.2.1 Water Temperature

The mean surface water temperature (^{0}C) for all the sites varied significantly (Table 4.1). The highest mean water temperature of 27.53 ± 2.341^{0}C was obtained at Kathini (S1) while the lowest of 24.93 ± 1.902^{0}C was recorded at Riakanau (S4). The monthly water temperature for Manyatta (S3) ranged from 22.23 to 27.63^{0}C and Riakanau (S4) had a monthly water temperature range of 21.53 to 27.10^{0}C. At Tumutumu (S5) the mean water temperature was 25.36 ± 1.536^{0}C, while the monthly temperature varied from 22.33 to 27.30^{0}C (Table 4.1 and Appendix I).

One way analysis of variance (ANOVA) showed a significant difference in surface water temperature between sites (p = 0. 044; df = 55). Tukey's HSD test for separation of means revealed that mean water temperature for Kathini varied significantly from mean water temperature observed at Riakanau (Table 4.1).

Table 4.1: Mean ± standard deviation and range values for physical parameters in Masinga reservoir recorded between January, 2013 and December, 2013. Means in same row with different superscripts are significantly different at $p < 0.05$ levels.

Parameter/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
Water temp (^{0}C)	27.53 ±2.34 ^{ac}	26.06 ± 3.04 ^{ab}	25.43 ± 1.71 ^{ab}	24.93 ± 1.90 ^{b}	25.36 ± 1.52 ^{ab}
Range	22.93 – 30.43	21.03 – 30.50	22.23 – 27.63	21.53 – 27.10	22.33 – 27.30
DO (Mg L^{-1})	4.66 ± 2.13 ^{a}	5.30 ± 1.84 ^{a}	5.36 ± 1.94 ^{a}	5.21 ± 1.89 ^{a}	5.35 ± 1.85 ^{a}
Range	1.07 – 8.73	1.17 – 7.94	1.23 – 8.63	1.27 – 8.70	1.23 – 8.78
Turbidity (NTU)	41.50 ±23.06 ^{a}	64.23 ±51.82 ^{a}	49.66 ±38.59 ^{a}	47.81 ^{a} ± 26.41 ^{a}	52.71 ^{a} ± 31.51 ^{a}
Range	6.13 – 67.50	5.13 – 114.67	6.30 – 104.67	8.70 – 86.27	10.57 – 95.90
EC (µS cm^{-1})	125.98 ±21.09 ^{a}	109.79 ±11.82 ^{a}	110.47 ±5.91 ^{a}	116.48 ±12.42 ^{a}	117. 33 ±19.32 ^{a}
Range	103.77 – 168.83	94.53 – 141.30	96.03 – 117.87	100.47 – 136.17	89.70 – 155.30
pH	7.88 ± 0.80 ^{a}	7.66 ±0.72 ^{a}	7.68 ± 0.67 ^{a}	7.51 ± 0.77 ^{a}	7.56 ± 0.75 ^{a}
Range	6.22 – 8.85	6.41 – 8.55	6.42 – 8.50	6.01 – 8.60	5.90 – 8.46

The significant difference could be attributed to the fact that around Riakanau sampling site there was more vegetation cover compared to the Kathini which is sparsely vegetated. Riakanau is also upstream of the River Tana. Therefore, Riakanau had the lowest mean surface water temperature during the study period. In all the five sites, the monthly water temperature varied with daily weather conditions with the lowest temperature (21.03 – 22.93^{0}C) recorded in the month of August, 2013 (Figure 4.1). The monthly variations in water temperature could be attributed to the seasonal dynamics of weather within the study area.

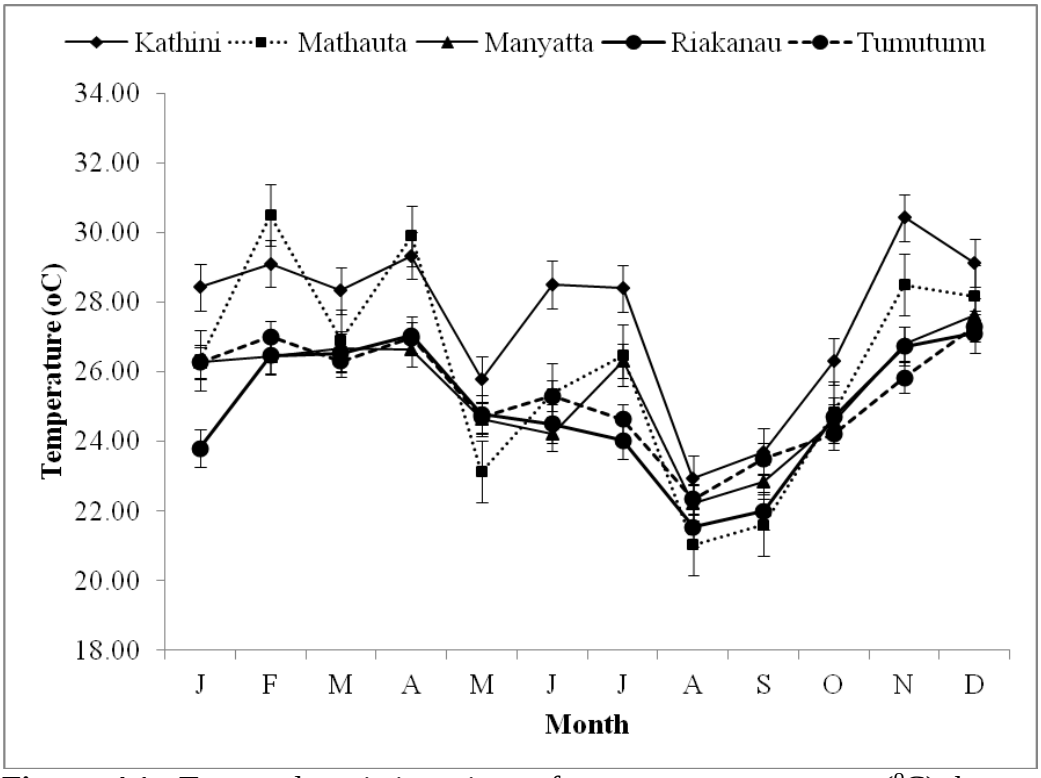

Figure 4.1: Temporal variations in surface water temperature (^{o}C) between January (J) and December (D) 2013 at different sampling sites within Masinga reservoir.

The water temperature recorded during this study compared well with other tropical waters and was within acceptable ranges for aquatic life in tropical ecosystems. Ajibade *et al.,* (2008) found the surface water temperature for major rivers of Kainji Lake National park, Nigeria to range between 22.6 – 31^0C while Kobingi *et al.,* (2009) observed at a mean temperature range of 23.2 – 25.2^0C in Kisian and Kisat Rivers in Lake Victoria drainage basin, Kenya. Raburu *et al*., (2009) while carrying out studies in the Lake Victoria basin found temperature range (23.43 – 24.23^0C) within impaired sites in River Nyando. Kitur (2009) obtained slightly lower water temperature (21.6 – 24.3^0C) in selected reservoirs in Central, Kenya while Kotut *et al.,* (1998a) recorded mean temperature range of 23.6 – 26.0^0C in Turkwel Gorge reservoir in Northern Kenya.

Temperature affects distribution, health and survival of aquatic organisms (Osman and Kloas, 2010). This is because temperature influences the amount of dissolved oxygen that is available to aquatic organisms and also the metabolic rate (APHA, 2005). The monthly water temperature range of 21.03^0C - 30.50^0C at the sampling sites (Figure 4.1) was within acceptable limits for warm water fish species found in Masinga reservoir.

4.2.2 Dissolved Oxygen (DO)

The mean dissolved oxygen concentrations (mg L^{-1}) for the different sampling sites showed modest variations (Table 4.1 and Figure 4.2). The DO at Kathini varied from 1.07 to 8.73 mg L^{-1} and had a mean concentration of 4.66 ± 2.134 mg

L^{-1}. At Mathauta DO ranged from 1.17 to 7.94 mg L^{-1} and with a mean of 5.30 ± 1.844 mg L^{-1}. Manyatta and Riakanau had a mean DO concentration of 5.36 ± 1.939 mg L^{-1} and 5.21 ±1.886 mg L^{-1} respectively. The DO concentration for Tumutumu was found to be 5.35 ± 1.847 mg L^{-1} and it ranged between 1.23 to 8.78 mg L^{-1} (Appendix II). One way ANOVA showed that there was no significant differences in the mean DO concentration between the sites ($p = 0.983$; $df = 55$).

Dissolved oxygen in surface water come from air or is produced by photosynthetic phytoplankton and other plants within a water body. DO is essential for almost all aquatic life and its concentration in a water body provides a broad indication of water quality. The level of DO in natural waters is strongly influenced by the water temperature. This means that high levels of DO are experienced when the water is coldest (Taseli, 2006). The temporal variations in DO levels in the sampling sites revealed that the lowest average mean DO levels were experienced in the month of May 2013 and the highest mean DO concentrations in August 2013 (Figure 4.2). The low levels of DO during the month of May 2013 could be due to turbidity in surface water of Masinga Reservoir during the long rainy season or removal by decomposing organic matter brought in by the rivers. Turbidity affects light penetration which in turn leads to low rate of photosynthesis by phytoplankton.

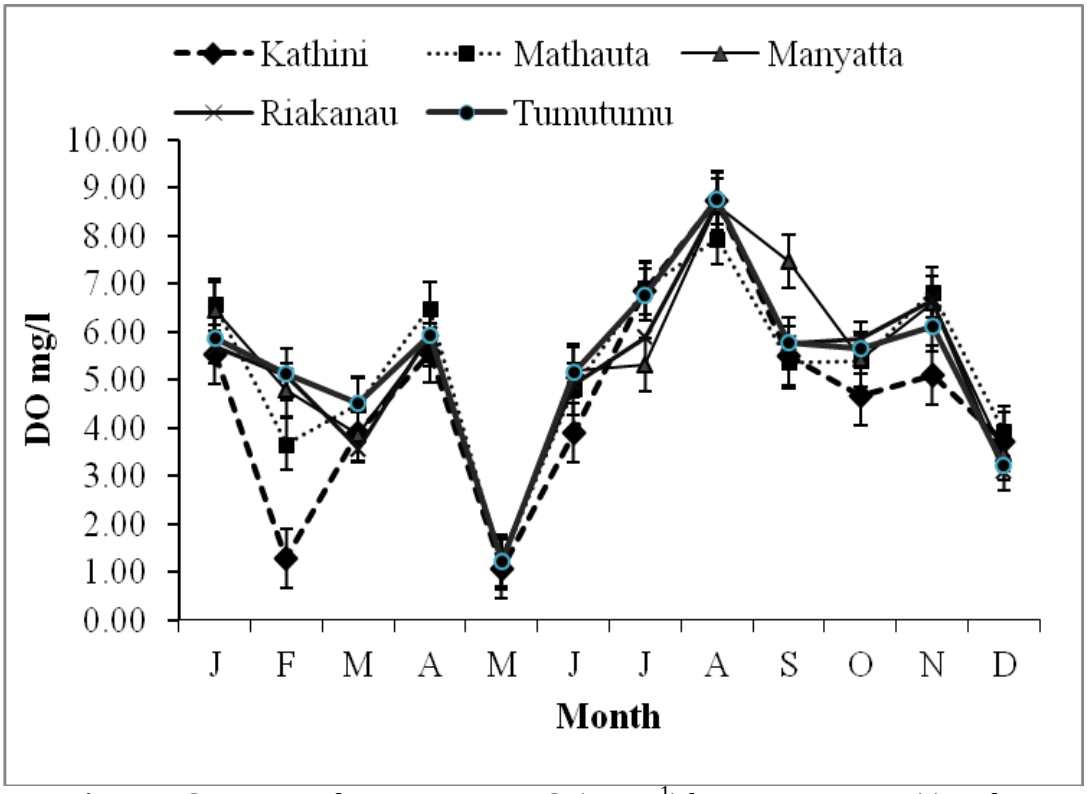

Figure 4.2: Temporal variations in DO (mg L^{-1}) between January (J) and December (D) 2013 in different sampling sites at Masinga reservoir.

Depletion of DO in water bodies is most frequent as a result of certain forms of water pollution (Srivastava *et al.,* 2009). According to Taseli (2006) the DO concentrations in unpolluted waters are typically in the range of 8 to 10 mgL^{-1} with concentrations below 5 mg L^{-1} known to adversely affect aquatic life. Kathini had slightly lower DO levels than other sampling sites and this could be due to cumulative effect of human activities within the Thika sub catchment. The sub catchment covers Thika town which is an industrial town and discharge of industrial wastes to Thika River could be a reason for low DO levels at Kathini sampling site.

The mean DO measured in this study is slightly lower compared with other studies done within the same geographical region. This could be due to high turbidity levels in Masinga reservoir and time of sampling. Kitur (2009) observed higher mean DO levels (6.2 – 9.0 mg L^{-1}) in five selected reservoirs in central Kenya. Kotut *et al.,* (1998a) obtained DO range of 4.9 – 9.2 mg L^{-1} in Turkwel Gorge reservoir while Ouma and Mwamburi (2014) recorded mean DO of 6.9 mg L^{-1} in Lake Baringo, Kenya.

4.2.3 pH

The mean pH levels recorded at different study sites showed moderate variations (Table 4.1). Kathini mean pH was (7.88 ± 0.794) and ranged from 6.22 – 8.85 while mean pH for Mathauta was (7.66 ± 0.724) with a range of 6.41 – 8.55. The mean pH level for Manyatta was (7.68 ± 0.671), Riakanau (7.51 ± 0.768) and 7.56 ± 0.749 was measured at Tumutumu. One way ANOVA revealed that there was no significant difference ($p = 0.767$, $df = 55$) in mean pH among the five sampling sites investigated. The monthly pH variations are recorded in Figure 4.3 and Appendix III.

The recorded mean pH values in all the sampling sites were within acceptable range for water used for human (6.5 – 8.5) and livestock consumption (EPA, 1997; 2002). pH measurements indicate the acidity or alkalinity of water. Naturally occurring fresh waters have a pH range between 6.0 and 8.0 (Osman and Kloas, 2010).

The pH of water is very important because it affects the solubility and availability of nutrients and their utilization by aquatic organisms (Osman and Kloas, 2010). The monthly pH measurements in this study indicated slightly alkaline water, except for the months of March and April, 2013 (Figure 4.3). Rainwater, which has a slightly acidic pH, as well as dilution effect, could be responsible for the decreased pH values in the months of March and April, 2013. The pH range within the study area was found out to be suitable for fisheries (EPA, 2002). In general the pH was within the limits of the standard values (APHA, 1999) and WHO guideline of 6.0 – 8.5 for drinking water quality (De, 2002 and Bbosa *et al.*, 2009). This pH range also indicates productive nature of a water body (Garg *et al.*, 2010).

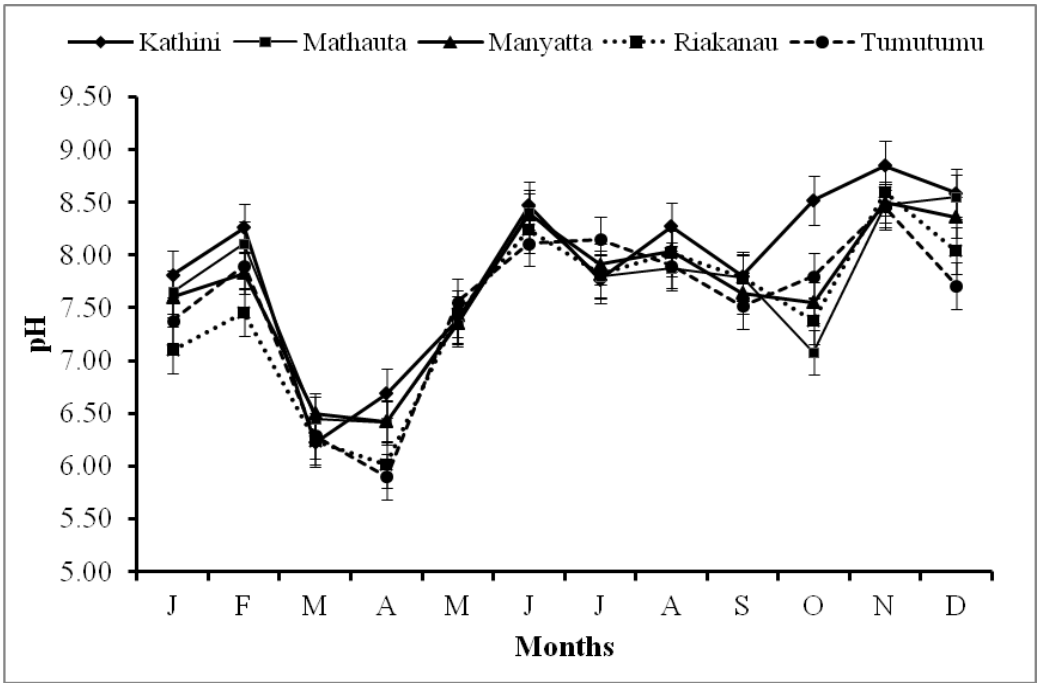

Figure 4.3: Temporal variations in pH between January (J) and December (D) 2013 in different sampling sites at Masinga reservoir.

The results obtained in this study are relatively similar to other physicochemical characteristics of water studies carried out in Kenya (Mkare *et al.,* 2010; Bouillon *et al.,* 2009; Kitur, 2009 and Kotut *et al.,* 1998a). Kotut *et al.,* (1998a) observed mean pH ranging from 6.7 – 8.9 in Turkwel Gorge reservoir while Kitur (2009) obtained mean pH range of 7.2 – 7.7 in selected reservoirs in central part of Kenya. Mkare *et al.,* (2010) observed a mean pH range of 7.2 – 7.89 at Chepkanga dam in Eldoret, Kenya and Bouillon *et al.,* (2009) obtained a pH value of 7.2 in Tana River just below Masinga reservoir. However, Ouma and Mwamburi (2014) obtained slightly higher pH levels (8.0 – 8.5) in Lake Baringo, Kenya and Pacini (1994) recorded a mean pH range of 8.0 – 8.6 in Kamburu dam.

4.2.4 Turbidity

Mean turbidity levels (NTU) obtained during the study period are shown in Table 4.1. The turbidity levels measured at Kathini was (41.50 ± 23.061), Mathauta (64.23 ± 51.817), Manyatta (49.66 ± 38.591), Riakanau (47.81 ±26.412) and Tumutumu (52.71 ± 31.512). One way ANOVA revealed that there was no significant difference in turbidity levels ($p = 0.624$, $df = 55$) between the sampling sites. The monthly turbidity levels in the sites are shown in Figure 4.4 and Appendix IV. Generally, there were wide variations in turbidity levels recorded at different months within each sampling site. The lowest monthly turbidity level observed was 6.13 NTU at Kathini while the highest value was 169.67 NTU at Mathauta in the month July 2013.

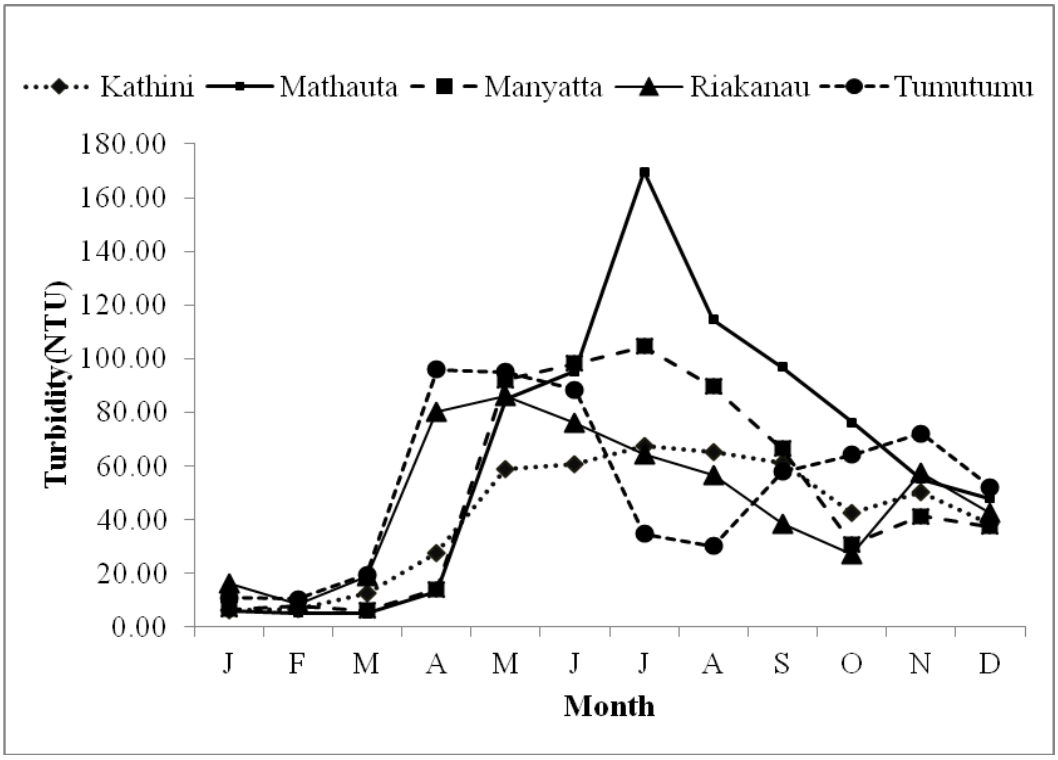

Figure 4.4: Temporal variations in turbidity (NTU) between January (J) and December (D) 2013 in different sampling sites at Masinga reservoir.

Turbidity is the cloudiness of a water body caused by suspended solids that are generally invisible to the naked eye (Ndimele and Kumolu-Johnson, 2012). Turbidity values less than 10 NTU represent very clear water, 50 NTU shows cloudy water and 100 – 500 NTU indicates very cloudy water (Barnes *et al*., 1998). The study showed Masinga reservoir has cloudy water, with higher turbidity levels than WHO guidelines (5 NTU) for drinking water (WHO, 2003). Turbidity affects light penetration through the water column and hence reducing primary productivity of a water body. Higher values were recorded during the raining season as compared to the dry season. This could be attributed to run off water from the catchments which carry suspended materials into the reservoir.

According to Chapman (1992), the concentration of suspended solids in a water body controls the turbidity of the water.

Poor farming practices around Masinga Reservoir and the upper catchments seems to have accelerated the high turbidity levels as recorded during the rainy seasons. The soils around Masinga Reservoir are bare and hence highly susceptible to erosion during the rainy seasons. Mathauta (S2) and Tumutumu (S5) had slightly higher turbidity levels than the rest of the sampling sites. These sites are located at the lower and upper reaches of the dam respectively. The vegetation cover in the sub-catchment that serves Mathauta with water is rangelands that are overgrazed coupled with poor land use practices. The land use practices around Tumutumu are also exhibited by poor farming methods. Tumutumu is also, served with the water from the loose soils of Murang'a County hence accelerating siltation into the reservoir through Tumutumu site.

The mean turbidity levels obtained during this study are comparable with those observed by Ouma and Mwamburi (2014) in Lake Baringo of mean value 43.3 NTU. Muyondi *et al.,* (2010) obtained lower turbidity levels of 2.25 – 8.88 NTU in the pelagic waters of Lake Victoria, while Mwamburi (2013) observed 6.0 – 56.1 NTU in Lake Victoria open waters. In Lake Naivasha mean turbidity ranging 30 – 120 NTU has been observed (Mwamburi, 2013).

4.2.5 Electrical Conductivity (EC)

The mean electrical conductivity levels during the study showed modest variations (Table 4.1). The mean EC at Kathini was (125.98 ±21.090 µS cm^{-1}), Mathauta (109.79 ±11.824 µS cm^{-1}), Manyatta (110.47 ± 5.908 µS cm^{-1}), Riakanau (116.48 ±12.422 µS cm^{-1}), and Tumutumu (117. 33 ± 19.319 µS cm^{-1}). Figure 4.5 shows the temporal variations in EC during the study period. The highest EC value was observed at Kathini (168.83 µS cm^{-1}) in September 2013 and the lowest was at Tumutumu (89.70 µS cm^{-1}) in June 2013 (Appendix V).

One way ANOVA showed that there was no significant difference ($p = 0.077$; $df = 55$) in EC mean levels between the sites. The temporal variations in conductivity could be attributed to water level fluctuation in the reservoir. Water level fluctuation in Masinga reservoir is mainly due to high usage of water for hydro electric power generation and irrigation by farmers during the dry seasons.

The mean EC recorded in Masinga reservoir were lower than 556 - 601µS cm^{-1} observed in Lake Baringo (Ouma and Mwamburi, 2014) and 270 - 305 µS cm^{-1} of Lake Naivasha (Mwamburi, 2013). Also, the mean EC was lower than what Oyoo *et al.,* (2009) measured in Lake Nakuru (3300 – 41,900 µS cm^{-1}) and 252.4 µS cm^{-1} in Garcas reservoir (Oliveria *et al.*, 2010). However, the EC was higher than 91 – 107 µS cm^{-1} observed in the open waters of Lake Victoria (Mwamburi, 2013) and 91.53 – 97.72 µS cm^{-1} in the pelagic waters of Lake Victoria (Muyondi *et al.,* 2010).

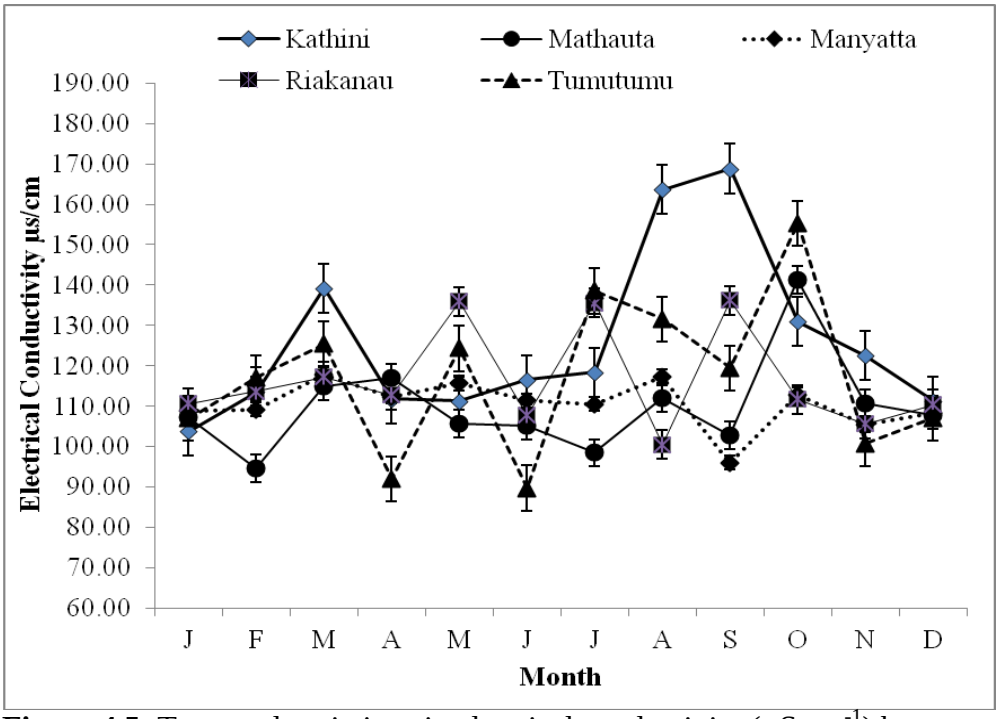

Figure 4.5: Temporal variations in electrical conductivity (µS cm^{-1}) between January (J) and December (D) 2013 in different sampling sites at Masinga reservoir.

Conductivity is the measure of capacity of a substance or solution to conduct electric current and is used to determine the total dissolved solids in water (Mushatq *et al.*, 2013). EC is a useful indicator of the mineralization in a water sample (Jain *et al.*, 2005). The World Health Organization (WHO) limit for EC for drinking and potable water is 700 µS cm^{-1} (WHO, 2003). Based on this limit, the Masinga reservoir water is suitable for domestic use in relation to electrical conductivity recorded in this study. According to Fatoki and Awofolu (2003), health effects in human beings for consuming water with high EC may include disturbances of salt and water balance, adverse effect on certain mycocardic patients and individuals with high blood pressure.

4.3 Heavy Metal Concentrations in Sediments

4.3.1 Copper (Cu) Concentration (mg kg^{-1} Dry Weight)

The mean Cu concentrations (mg kg^{-1}) at the five sampling sites showed modest variations (Table 4.2). The mean Cu concentrations were Riakanau (11.38 ± 2.77 mg kg^{-1}), Kathini (14.19 ± 6.986 mg kg^{-1}), Manyatta (18.21 ± 9.45 mg kg^{-1}), Mathauta (19.08 ± 6.82 mg kg^{-1}) and Tumutumu (23.67 ± 6.54 mg kg^{-1}). One way ANOVA revealed significant differences ($p = 0.00$; $df = 55$) between the sites (Table 4.2). Tukey's HSD test showed that Cu concentration levels recorded at Kathini was significantly different from Tumutumu, but not significantly different from the other three sites. Tumutumu showed significant difference in Cu concentration levels with Riakanau and Kathini, but no significant variation with Mathauta and Manyatta.

The temporal variations in Cu concentrations during the study period are indicated in Table 4.3. The highest levels of Cu concentrations were recorded at Tumutumu during the month of May 2013 (34.64 mg kg^{-1}) and the lowest at Kathini (5.20 mg kg^{-1}) in February 2013. Copper can get into aquatic ecosystems from diverse sources for example, from Cu compounds used in fungicides, algicides, insecticides, wood preservatives, electroplating and azo dye manufacture (Akan *et al.*, 2010). Also, from Cu compounds added in fertilizers and animal feeds as a nutrient to support plant and animal growth.

Table 4.2: Mean ± standard deviation and range values for heavy metal concentrations in sediments recorded from January – December 2013 in Masinga reservoir. Means in same row with different superscripts are significantly different at $p < 0.05$ levels. ND – Below detectable limit

Element/ Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
Cu (mg kg^{-1})	14.19 ± 6.986^{a}	19.08 ± 6.822^{ab}	18.21 ± 9.448^{ab}	11.38 ± 2.770^{a}	23.67 ± 6.543^{b}
Range	5.20 – 25.03	9.58 – 32.95	6.50 – 31.75	8.00 – 16.37	15.00 – 34.64
Zn (mg kg^{-1})	75.84 ± 27.684^{a}	71.35 ± 29.874^{a}	65.81 ± 21.688^{a}	60.04 ± 25. 633^{a}	69.49 ± 22.434^{a}
Range	5.20 – 91.07	20.00 – 80.90	10.23 – 82.90	24.42 – 64.55	32.00 – 100.35
Pb (mg kg^{-1})	12.03 ± 5.650^{a}	13.85 ± 9.488^{a}	11.14 ± 5.177^{a}	12.04 ± 5.652^{a}	14.47 ± 6.463^{a}
Range	4.25 – 22.63	4.68 – 32.23	3.07 – 17.83	4.15 -24.23	4.45 – 24.68
Cr (mg kg^{-1})	31.94 ± 11.800^{b}	21.39 ± 6.540^{b}	37.40 ±21.236^{a}	24.93 ± 9.806^{b}	49. 62 ± 14.742^{a}
Range	7.50 – 43.80	15.50 – 32.30	15.50 – 77.60	11.70 – 39.58	32.90 – 77.10
Mn (mg kg^{-1})	642.39 ± 225.346^{a}	514.91 ± 275.302^{a}	606.57 ± 276.864^{a}	259.12 ± 92.033^{b}	603.26 ± 276.399^{a}
Range	287.50 – 831.25	242.92 – 823.75	297.50 – 888.75	138.75 – 351.25	319.58 - 937.
Cd (mg kg^{-1})	ND	ND	ND	ND	ND

Copper compounds are also used in food additives and copper salts in water supply systems to control biological growths in reservoirs and distribution pipes (Eaton, 2005; WHO, 2004). Copper is an essential substance to human life, however, in high concentrations, it can cause anaemia, liver and kidney damage, stomach and intestinal irritation (Turnlund, 1998). The high Cu levels in Tumutumu could be attributed to agricultural activities in the catchment especially the use fertilizers, fungicides and insecticides. The catchment that covers Murang'a, Maragua, Sagana and Karatina, is a high potential area for agriculture, both dairy and crops. Therefore, during the rainy season Cu compounds added in fertilizers and animal feeds get into Masinga reservoir through surface runoff.

The mean levels of Cu in the study area were below the WHO standard values of 25 mg kg^{-1} for the survival of aquatic organisms (WHO, 2004), however on the temporal scale slightly higher values were observed (Table 4.3). This was mainly during the rainy seasons. Comparable mean Cu Concentration levels in surface sediments have been observed in five Rift Valley Lakes (Nakuru, Naivasha, Elementaita, Bogoria and Baringo) in Kenya with a mean ranging from 1.46 – 20.95 mg kg^{-1} (Ochieng *et al.,* 2007). In Lake Kanyaboli, mean Cu concentration levels ranging from 1.80 – 30.27 mg kg^{-1} have been observed (Ochieng *et al.,* 2008). Heavy metal contamination studies done in Lake Victoria (Winam Gulf) found higher mean levels of Cu in surface sediments (3.90 – 150.2 mg kg^{-1}) than obtained in Masinga reservoir (Ochieng *et al.,* 2008). Other studies carried out have revealed lower mean Cu levels in sediments, for example Tono Irrigation

Reservoir (0.25 mg kg^{-1}), Ghana (Anim-Gyampo *et al.*, 2013) and River Nile (0.024 – 0.054 mg kg^{-1}), Egypt (Osman and Kloas, 2010) and Lake Victoria (3.31 – 3.44 mg kg^{-1}), Kenya (Oyoo-Okoth *et al.,* 2010). Saeed and Shaker (2008) obtained higher Cu levels in sediments in the Northern Delta Lakes (36.77 – 315.36 mg kg^{-1}), Egypt.

4.3.2 Zinc (Zn) Concentration (mg kg^{-1} Dry Weight)

The mean concentration levels for Zn (mg kg^{-1}) recorded during the study in different sites showed variations (Table 4.2). The mean concentrations for Riakanau was 60.04 ± 25.633 mg kg^{-1}, 75.84 ± 27.684 mg kg^{-1} for Kathini, 71.35 ± 29.874 mg kg^{-1} at Mathauta, 61.81 ± 21.688 mg kg^{-1} for Manyatta and 69.49 ± 22.434 mg kg^{-1} at Tumutumu. There was no significant difference ($p = 0.632$; $df = 55$) in Zn levels between the different sites. The monthly average Zn levels recorded at different sampling sites are shown in Table 4.3.

The source of Zn concentrations in sediments to reservoirs could be from a number of alloys including brass and bronze, batteries, fungicides and pigments (Akan *et al.,* 2010). Zinc is also used in galvanizing steel and iron products hence a possible source from the urban areas within the Masinga reservoir catchment. Another source could be Zn Carbonates used as pesticides (Anglin-Brown *et al.*, 1995) and textile industries' waste waters (Smith, 1988). The elevated Zn values recorded at Kathini may be attributed to Zn which is used in printing and dyeing processes in textile industries located within the Thika sub catchment.

Table 4.3: Temporal variations of heavy metals (mg kg^{-1}) in sediments at difffernt samplimg sites during the study period

Site/Month	Element	Jan	Feb	March	April	May	June	July	August	Sept	Oct	Nov	Dec
Kathini	Cu	6.34	5.20	25.03	3.50	20.35	19.53	14.45	10.75	9.58	17.28	17.70	20.60
	Zn	8.50	5.20	56.33	10.25	60.51	66.41	91.07	42.25	38.08	67.11	37.70	52.40
	Pb	11.52	8.20	9.03	4.25	6.90	9.20	10.45	11.50	13.00	15.49	22.63	22.25
	Cr	43.80	40.27	41.78	7.50	35.68	39.00	43.03	18.25	15.50	33.96	33.95	30.55
Mathuata	Cu	16.06	16.00	25.97	13.00	25.06	22.83	16.67	10.75	9.58	18.13	32.95	23.98
	Zn	33.67	24.43	30.13	20.00	47.83	51.75	76.45	42.25	38.08	48.50	47.33	80.90
	Pb	31.37	5.48	5.28	11.17	5.13	11.82	4.68	11.50	13.00	17.88	32.23	16.68
	Cr	22.30	17.80	17.90	19.75	16.13	16.78	16.81	18.25	15.50	32.03	31.15	32.30
Manyatta	Cu	6.50	9.20	31.75	12.42	29.17	31.59	21.91	10.75	9.58	8.93	25.75	23.95
	Zn	19.47	10.23	48.23	25.33	67.01	62.66	82.90	42.25	38.08	73.43	76.68	68.18
	Pb	7.00	3.07	4.83	8.50	16.12	15.96	5.60	11.50	13.00	13.38	17.83	16.95
	Cr	20.40	19.87	22.80	17.42	37.65	47.69	77.60	18.25	15.50	56.68	59.33	55.60
Riakanu	Cu	9.93	7.53	16.37	8.00	10.93	14.29	10.28	9.75	9.08	12.10	14.28	15.05
	Zn	38.77	32.80	36.53	24.42	41.86	57.08	64.55	26.75	25.08	45.50	57.15	56.10
	Pb	7.30	8.43	5.18	13.50	13.57	17.23	8.78	15.25	14.42	12.43	4.15	24.23
	Cr	20.40	11.70	34.90	14.25	27.55	29.55	39.58	14.75	13.17	25.50	35.10	32.70
Tumutumu	Cu	15.00	21.07	28.90	16.25	34.64	34.20	24.56	16.42	18.83	23.83	26.88	27.43
	Zn	33.23	47.53	55.63	32.00	75.75	70.82	80.16	38.50	36.25	91.00	72.30	100.35
	Pb	16.33	16.97	5.53	8.75	15.51	12.75	4.45	12.08	12.33	22.50	21.80	24.68
	Cr	35.27	32.90	53.86	34.25	58.38	50.67	51.05	36.67	40.83	73.48	50.95	77.10

The results obtained on mean Zn concentration levels in all the sampling sites did not exceed the WHO recommended limit of 123 mg kg^{-1} (WHO, 2008). However, sediments have the capacity to accumulate more heavy metals with time and remobilize them back to water and the food chain (WHO, 2008). Compared to other studies, mean Zn levels in Masinga reservoir were lower than 96.2 to 229.6 mg kg^{-1} recorded in five Rift Valley lakes, Kenya (Ochieng *et al.,* 2007). However, they were within the mean Zn levels recorded in Lake Kanyaboli (65.0 – 146 mg kg^{-1}) and 23.39 – 350.80 mg kg^{-1} at Winam gulf (Ochieng *et al.*, 2008).

4.3.3 Lead (Pb) Concentration (mg kg^{-1} Dry Weight)

The mean Pb concentration levels recorded in sediment in different sampling sites during the study showed modest variations (Table 4.2). They ranged from 11.14 ± 5.177 mg kg^{-1} in Manyatta to 14.47 ± 6.463 mg kg^{-1} in Tumutumu. The mean Pb levels for the other sites were Kathini (12.03 ± 5.650 mg kg^{-1}), Mathauta (13.85 ± 9.488 mg kg^{-1}) and Riakanau (12.04 ± 5.652 mg kg^{-1}) Analysis of variance (ANOVA) revealed no significant difference between the different sites ($p = 0.719$; $df = 55$). The monthly Pb levels showed moderate variations between the months in each sampling site (Table 4.3).

The sources of Pb in sediments include industrial wastes and from water pipes (Akan *et al.,* 2010). Other likely sources of Pb are lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors, ammunition, glazes and plastic stabilizers (WHO, 2004). The consequences of excess lead in the human body

range from low intelligent quotient in children and high blood pressure in adults (Ottaway, 1978). In addition lead can produce a damaging effect on the kidney, liver and nervous system, blood vessels and other tissues (Sharma and Pervez, 2003).

The levels of Pb concentrations observed in Masinga reservoir were lower than the recommended limit of 35mg kg^{-1} for Pb in sediment (WHO, 2004). Mean Pb levels in Masinga reservoir (11.14 – 14.47 mg kg^{-1}), were within the range recorded in Rift Valley lakes of 10.92 – 38.98 mg kg^{-1} (Ochieng *et al.*, 2007). Ochieng *et al.*, (2008) found higher mean levels of Pb in sediments of different sites within Lake Kanyaboli (11.42 – 153.90 mg kg^{-1}) and Winam Gulf (3.09 – 66.05 mg kg^{-1}).

4.3.4 Chromium (Cr) Concentration (mg kg^{-1} Dry Weight)

The mean Cr concentrations observed in sediments during the study are shown in Table 4.2. The mean Cr concentrations at different sites were 21.39 ± 6.540 mg kg^{-1} (Mathauta), 49.62 ±14.742 mg kg^{-1}(Tumutumu), 31.94 ± 11.800 mg kg^{-1}(Kathini), 37.40 ± 21.236 mg kg^{-1}(Manyatta) and 24.93 ± 9.806 mg kg^{-1}(Riakanau). The monthly Cr concentrations within the study area are shown in Table 4.3. Using one ANOVA it was found there was significant difference ($p = 0.00$; $df = 55$) in the levels of mean Cr between the sampling sites. Tukey's HSD test showed that mean Cr levels recorded at Tumutumu and Manyatta were significantly higher than Cr levels observed at Kathini, Mathauta and Riakanau.

Sources of Cr in aquatic ecosystems are attributed to industrial and sewage wastes (Akan *et al.,* 2010). Therefore, the high mean Cr levels at Tumutumu could be due to industrial wastes and sewage from the towns located within the catchment. The mean Cr concentration obtained at Tumutumu was higher than the recommended limit of 37.5 mg kg^{-1} for Cr in sediments (WHO, 2008). Chromium concentration levels in sediments of Manyatta were slightly lower (37.40 ± 21.236 mg kg^{-1}) than the recommended limit. Also, the study revealed that during the rainy seasons the levels of Cr were higher and exceeded the recommended limits. During the rainy season, a lot of industrial wastes get into water channels through surface run off causing elevated levels in sediments. Chromium and its compounds are known to cause cancer of the lung, nasal cavity and suspected to cause cancer of the stomach and larynx (ATSDR, 2000). For Cr concentrations exceeding 25 mg kg^{-1}, a condition known as allergic dermatitis could occur (EPA, 1999).

Chromium mean levels in Masinga reservoir were higher than 0.42 – 1.12 mg kg^{-1} recorded in sediments of Lake Victoria, Kenya (Oyoo-Okoth *et al.*,2010) but lower than 31.54 – 165.01 mg kg^{-1} at different reservoirs, Switzerland (Wildi *et al.,* 2004). Other studies that have recorded higher mean Cr levels are for example off Bushehr, Persian Gulf 130.5 mg kg^{-1} (Karbassi *et al.,* 2005) and Danube river, Serbia 30.6 – 112.5 mg kg^{-1} (Milenkovic *et al.,* 2005).

4.3.5 Manganese (Mn) Concentration (mg kg^{-1} Dry Weight)

Mn concentrations recorded during the study in sediments are indicated in Table 4.2. The lowest mean Mn concentration was 259.12 ± 92.033 mg kg^{-1} (Riakanau) while the highest mean Mn was recorded at Kathini (642.39 ± 225.346 mg kg^{-1}). Tumutumu had mean Mn level of 603.26 ± 276.399 mg kg^{-1}, Manyatta (606.57 ± 276.864 mg kg^{-1}) and Mathauta (514.91 ± 275.302 mg kg^{-1}). One way ANOVA showed that Mn level observed at Riakanau (259.12 ± 92.033 mg kg^{-1}) was significantly lower compared to those obtained in other sites ($p = 0.00$; $df = 25$). The temporal variations in Mn Concentration levels in the sampling sites are shown in Appendix VII.

Manganese is known to be a very abundant element widely distributed in the earth's crust. It is used in manufacturing of dry cell batteries, glass, and fertilizer and in the leather and textile industries. Masinga reservoir catchment has several textile industries based at Thika town and a lot of fertilizer is used in the agricultural sector within the catchment. These could be the likely sources of Mn to Masinga reservoir. Also, Mn is released into the atmosphere by both natural and anthropogenic processes, mostly in form of coarse particles, through wind erosion and road dusts. It is also released through agricultural activities, building activities and quarry processes (Ziemacki *et al.,* 1989).

The mean Mn levels observed in this study were lower compared to other studies done else in Kenya. For example, Ochieng *et al.,* (2007) recorded higher mean Mn

levels in sediments of five rift valley lakes (667.7 – 3,946.8 mg kg^{-1}) and Lake Kanyaboli (1073 – 2,629 mg kg^{-1}). However, Lalah *et al.,* (2008) recorded almost similar mean Mn levels (133.5 – 723.7 mg kg^{-1}) in sediments sampled from Winam Gulf, Lake Victoria. Osman and Kloas (2010) found slightly lower mean Mn levels (159.84 – 351.79 mg kg^{-1}) in sediments sampled along the course of River Nile, Egypy. Saeed and Shaker (2008) recorded mean Mn levels of 419.60 ± 29.99 mg kg^{-1} and 850.95 ± 63.96 mg kg^{-1} in sediments of Lake Manzala and Lake Borollus, Egypt respectively.

4.4 Heavy Metal Concentrations in Surface Water

4.4.1 Copper (Cu) Concentration (mg L^{-1})

The mean concentrations of Cu (mg L^{-1}) in surface water from all sampling stations varied (Table 4.4). The mean Cu concentrations recorded were 0.003 ± 0.002 mg L^{-1} (Riakanau), 0.006 ± 0.003 mg L^{-1} (Kathini), 0.008 ± 0.003 mg L^{-1} (Tumutumu), 0.018 ± 0.007 mg L^{-1} (Manyatta) and 0.019 ± 0.003 mg L^{-1} (Mathauta). One way ANOVA showed that there was no significant variation ($p = 0.109$; $df = 55$) in Cu concentrations levels between the different sampling sites. Copper is a natural element which is widely distributed in soils, rocks and in rivers. It is released into water as a result of natural weathering of soil and discharges from industries and sewage treatment plants (Romo-Kroger *et al.,* 1994 and Hutchinson,2002). Copper in surface water is from extensive use of pesticides sprays which contain Cu compounds for agricultural purposes (Al-Weher, 2008).

Table 4.4: Mean ± standard deviation and range values for heavy metal concentration (mg L^{-1}) in surface water of Masinga reservoir from January – December 2013. Means in same row with different superscripts are significantly different at $p < 0.05$ levels. ND – Below detectable limit

Element/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
Cu (mg L^{-1})	0.006 ± 0.003 [a]	0.019 ± 0.009 [a]	0.018 ± 0.007 [a]	0.003 ± 0.002 [a]	0.008 ± 0.003 [a]
Range	Nd – 0.026	Nd – 0.057	Nd – 0.073	Nd -0.020	Nd – 0.024
Zn (mg L^{-1})	0.092 ± 0.013 [a]	0.109 ± 0.018 [a]	0.132 ± 0.019 [a]	0.108 ± 0.018 [a]	0.111 ± 0.019 [a]
Range	0.046 – 0.184	0.056 – 0.282	0.062 – 0.255	0.060 – 0.262	0.071 – 0.291
Pb (mg L^{-1})	0.009 ± 0.005 [a]	0.005 ± 0.002 [a]	0.004 ± 0.001 [a]	0.004 ± 0.002 [a]	0.005 ± 0.002 [a]
Range	Nd -0.063	Nd – 0.023	Nd – 0.015	Nd – 0.023	Nd – 0.021
Cr (mg L^{-1})	0.003 ± 0.002 [a]	0.005 ± 0.005 [a]	0.003 ± 0.001 [a]	0.006 ± 0.004 [a]	0.006 ± 0.003 [a]
Range	Nd – 0.028	Nd – 0.058	Nd – 0.013	Nd – 0.042	Nd – 0.039
Mn (mg L^{-1})	0.085 ± 0.084 [a]	0.006 ± 0.005 [a]	0.038 ± 0.037 [a]	0.012 ± 0.006 [a]	0.146 ± 0.046 [a]
Range	Nd – 0.504	Nd – 0.033	Nd – 0.221	Nd – 0.031	0.003 – 0.348
Cd (mg L^{-1})	ND	ND	ND	ND	ND

In the dissolved form, Cu is potentially very toxic to aquatic animals and plants, especially to young life-stages such as fish larvae. However, the toxicity is greatly reduced when Cu is bound to particulate matter in the river water and when the water is hard (Damodharan, 2013). The mean Cu levels obtained in this study were lower compared to 0.69 – 0.94 mg L^{-1} observed in surface waters of Lake Victoria, Kenya (Oyoo-Okoth *et al.,* 2010). However, they were within same range 0.005 – 0.01mg L^{-1} of mean Cu levels recorded in five Rift Valley lakes in Kenya (Ochieng *et al.,* 2007). Studies by Ochieng *et al.,* (2008) found higher mean Cu levels 0.012 – 0.043 mg L^{-1} in surface water of Lake Kanyaboli, Kenya. The mean Cu levels obtained in Masinga reservoir did not exceed the WHO limits of 1.00 mg L^{-1} of Cu concentration in water for drinking (WHO, 2004).

4.4.2 Zinc (Zn) Concentration (mg L^{-1})

The mean Zn concentration levels in surface water for all the sampling sites are presented in Table 4.4. The mean Zn levels recorded ranged from 0.092 ± 0.013 mg L^{-1}(Kathini), 0.108 ± 0.018 mg L^{-1} (Riakanu), 0.109 ± 0.018 mg L^{-1} (Mathauta), 0.111 ± 0.019 mg L^{-1} (Tumutumu) and 0.132 ± 0.019 mg L^{-1} (Manyatta). The results indicated no significant difference in mean Zn concentration levels ($p = 0.619$; $df = 55$) among the different sampling stations.

Zn is introduced into water bodies through artificial pathways such as by-products of steel production or coal-fired power stations and burning of waste materials (Damodharan, 2013). It is also through leaching from fertilizers, effluents of

commercial industries during mining and smelting (metal processing) activities. Other sources of Zn into aquatic ecosystems include urban runoff and municipal sewages (Damodharan, 2013). Zn is an essential nutrient for body growth and development; however drinking water containing high levels of zinc can lead to stomach cramps, nausea and vomiting. The concentration of Zn in surface water recorded in this study did not exceed the recommended limit of 3 mg L^{-1} for Zn levels in drinking water (WHO, 2008).

Similar studies done in Lake Victoria, Kenya have recorded Zn concentration levels as high as 0.220 mg L^{-1} (Lalah *et al.*, 2008 and Mwamburi, 2009). Also, Muiruri *et al.*, (2013) observed higher mean Zn levels (0. 055 – 0.695 mg L^{-1}) in Athi River tributaries. Ochieng *et al.*, (2007) observed mean Zn levels ranging 0.029 – 0.235 mg L^{-1} in five rift valley lakes (Nakuru, Naivasha, Baringo, Elementaita and Bogoria). At Lake Kanyaboli mean Zn levels in surface water ranging from 0.015 – 0.056 mg L^{-1} have been recorded (Ochieng *et al.*, 2008). Olatunji and Osibanjo (2012) obtained higher mean Zn levels (1.98 – 4.03 mg L^{-1}) in River Niger, North Central Nigeria compared to those observed in Masinga reservoir. Fahmy and Fathi (2011) obtained higher Zn levels in Wetland Lake, Al-Asfar, Saudi Arabia.

4.4.3 Lead (Pb) Concentration (mg L^{-1})

Mean Pb concentration levels in surface water showed modest variations (Table 4.4). The lowest mean Pb levels were recorded in Manyatta 0.004 ± 0.001 mg L^{-1}

and Riakanau 0.004 ± 0.002 mg L^{-1} while the highest mean Pb level was observed at Kathini 0.009 ± 0.005 mg L^{-1}. Mathauta and Tumutumu had similar mean Pb levels of 0.005 ± 0.002 mg L^{-1}. One way ANOVA revealed no significant difference ($p = 0.817$; $df = 55$) in Pb levels among the sampling sites.

Lead concentration in natural water increases mainly through anthropogenic activities (Geol, 1997). Hence, likely source of Pb in water bodies is from soil erosion, municipal and industrial wastes and run off (DWAF, 1996). Soil erosion within Masinga reservoir catchment coupled with municipal waste discharges could be the source of Pb levels observed in this study. Kathini sampling site had slightly higher Pb levels than other sites and this could be attributed to industrial effluents discharged into Thika River from manufacturing industries within the Thika town.The Pb levels observed in all the sampling sites were lower than the recommended limit of 0.01mg L^{-1} in drinking water (WHO, 2008). This means that the water in Masinga reservoir is not polluted by Pb.

Studies done elsewhere in Kenya indicate higher Pb concentration levels. For example Oyoo-Okoth *et al.,* (2010) found mean Pb levels ranging from 0.26 – 0.99 mg L^{-1} in Lake Victoria. Muiruri *et al.,* (2013) also, recorded lower and higher mean Pb levels at different sites (nd – 0.047 mg L^{-1}) in surface water of Athi River tributaries. Other studies that recorded higher mean Pb levels include open waters of Winam gulf (0.2 mg L^{-1}), River Nyando (0.19 mg L^{-1}), and 0.015 mg L^{-1} in River Sondu Miriu (Tole and Shitsama, 2003). Ochieng *et al.,* (2007)

obtained higher mean Pb levels ranging 0.025 – 0.563 mg L^{-1} in surface water of five Rift valley Lakes. Ochieng *et al.,* (2008) recorded Pb concentration levels of 0.006 – 0.048 mg L^{-1} in Lake Kanyaboli, Kenya. Studies carried out by Olatunji and Osibanjo (2012) also recorded higher mean Pb levels (0.02 – 0.04 mg L^{-1}) in surface water of River Niger, Nigeria.

4.4.4 Chromium (Cr) Concentration (mg L^{-1})

The mean Cr concentration levels recorded at different sampling sites during the study period are shown in Table 4.4. The mean Cr levels ranged from 0.003 ± 0.001 mg L^{-1} (Manyatta) to 0.006 ± 0.004 mg L^{-1} (Riakanau). Mean Cr level at Tumutumu was 0.006 ± 0.003 mg L^{-1}, Mathauta 0.005 ± 0.005 mg L^{-1} and 0.003 ± 0.002 mg L^{-1} (Kathini). The Cr levels at the different sampling sites showed no significant variations ($p = 0.955$; $df = 55$). The main sources of Cr are industrial wastes such as Cr pigment, tannery wastes, leather manufacturing wastes and municipal sewage sludge (Rahman *et al.,* 2012). In this study, the elevated Cr levels at Tumutumu and Riakanau could be attributed to municipal and tannery wastes from the towns located in the upper Masinga reservoir catchment. The mean Cr levels obtained in this study did not exceed the recommended limit of 0.05 mg L^{-1} for Cr in drinking water (WHO, 2008).

Compared to other studies, the mean Cr levels in surface water of Masinga reservoir were lower than 0.23 – 0.79 mg L^{-1} recorded in Lake Victoria (Oyoo-Okoth *et al.,* 2010), 0.025 – 0.188 mg L^{-1} in five rift valley lakes (Ochieng *et al.,*

2007) and 0.068 mg L^{-1} in Athi River tributaries (Muiruri *et al.,* 2013). Ochieng *et al.,* (2008) found mean Cr levels of 0.005 – 0.061mg L^{-1} at different sites in Lake Kanyaboli. Olatunji and Osibanjo (2012) recorded a much higher mean Cr levels of 1.19 – 3.16 mg L^{-1} in River Niger, Nigeria compared to Cr levels in Masinga reservoir. A higher mean Cr level of 0.049 ± 0.02 mg L^{-1} has been recorded in Owen multi-purpose dam water, Nigeria (Oyhakilome *et al.,* 2012). However, mean Cr levels observed at Masinga reservoir were within the range of 0.003 – 0.088 mg L^{-1} recorded in River Nile, Egypt (Osman and Kloas, 2010).

4.4.5 Manganese (Mn) Concentration (mg L^{-1})

Mean Mn concentration levels observed in this study showed modest variation and are presented in Table 4.4. The mean Mn concentration ranged from 0.006 ± 0.005 mg L^{-1} (Mathauta) to 0.146 ± 0.046 mg L^{-1} (Tumutumu). Kathini had the second highest mean Mn level (0.085 mg L^{-1}) in surface water while Manyatta and Riakanau had 0.038 mg L^{-1} and 0.012 mg L^{-1} respectively. One way ANOVA showed that there was no significant difference ($p = 0.199$; $df = 25$) in Mn levels in surface water at the different sampling sites. In all the sampling sites the mean Mn concentration levels in surface water was found to be lower that recommended limit of 0.40 mg L^{-1} for Mn in drinking water (WHO, 2008).

Manganese is an abundant metal in earth's crust and usually occurrs with iron. It is used in the manufacture of iron and steel alloys, as an oxidant for cleaning, bleaching and disinfection (as potassium permanganate) and as an ingredient in

various products (WHO 2011). Manganese is released into the atmosphere by both natural and anthropogenic processes, mostly in form of coarse particles, through wind erosion, road dusts, agricultural and building activities and quarry processes (Ziemacki *et al.,* 1989). It gets into the aquatic ecosystems from industries manufacturing dry-cell batteries, glass, and fertilizer and in leather and textile. The high levels observed at Kathini could be due to industrial activities in the Thika sub catchment while at Tumutumu the Mn levels recorded may be due to high use of agricultural fertilizers, soil erosion and quarry activities within the catchment.

Comparable studies carried out in Kenya have recorded higher mean Mn values than observed in Masinga reservoir. These studies include those done by Lalah *et al.,* (2008) in Winam Gulf, Lake Victoria (0.05 – 3.276 mg L^{-1}) and Ochieng *et al.,* (2008) in Lake Kanyaboli, Kenya (0.185 – 0.376 mg L^{-1}). Also, Ochieng *el al.,* (2007) obtained higher mean levels of Mn in five rift valley lakes (0.050 – 0.282 mg L^{-1}). Akoto *et al.,* (2008) recorded similar mean Mn values ranging from 0.099 – 0.140 mg L^{-1} in Owabi reservoir, Ghana while Mahadev and Gholami (2010) in KRS reservoir, India observed (0.0001 – 0.107 mg L^{-1}) and Osman and Kloas (2010) in River Nile, Egypt (0.033 – 0.099 mg L^{-1}). Oyhakilome *et al.,* (2012) recorded higher Mn Values (0.346 ± 0.391 mg L^{-1}) in Owen multi-purpose dam water, Nigeria.

4.5 Heavy Metal Concentrations in Selected Food Fish Species

The length (m) and weight (g) of fish samples at different sites is presented in Table 4.5. The mean weight for Tilapia sampled ranged from 94.18 ± 46.38 g (Tumutumu) to 235.74 ± 121.85 g (Manyatta), while African Catfish weight ranged from 366.53 ± 196.13 g (Tumutumu) to 626.40 ± 687.03 g (Manyatta). The lowest mean weight for Common Carp was recorded at Riakanau (374.03 ± 264.17g) and the highest was 581.05 ± 231.78 g at Manyatta.

4.5.1 Copper (Cu) Concentration (mg kg^{-1} Dry Weight)

The mean Cu levels recorded for muscles of Common Carp were 0.519 ± 0.426 mg kg^{-1} at Manyatta, 0.675 ± 0.065 mg kg^{-1} (Tumutumu), 1.054 ± 1.063 mg kg^{-1}(Riakanau), 1.087 ± 1.486 mg kg^{-1} (Mathauta) and 1.422 ± 1.299 mg kg^{-1} at Kathini (Table 4.6). One way analysis of variance indicated that there was no significant variation ($p = 0.254$; $df = 55$) of Cu levels between the sites (Figure 4.6). The monthly Cu levels varied moderately in different months (Appendix VIII) and the highest value (3.53 mg kg-1) was recorded at Riakanau in the month of March 2013.

Mean Cu levels recorded in African Catfish *Clarias gariepinus* during the study are shown in Table 4.7. The levels ranged from 0.677 ± 0.465 mg kg^{-1} (Manyatta) to 0.974 ± 1.284 mg kg^{-1} (Riakanau). The other mean Cu levels recorded were 0.896 ± 0.868 mg kg^{-1} (Kathini), 0.949 ± 0.697 mg kg^{-1} (Mathauta) and 0.791 ± 0.855 mg kg^{-1} (Tumutumu). The results exhibited no significant difference (p =

0.767; df = 55) in Cu levels recorded at different sampling sites (Figure 4.6). The temporal variations in Cu concentration levels recorded in Catfish muscles on different months are shown in Appendix IX. Mean Cu concentration levels in Tilapia *Oreochromis spirulus niger* for the five sampling sites varied (Table 4.8). The highest Cu levels were recorded at Kathini (0.782 ± 0.327 mg kg^{-1}) while the lowest levels were recorded at Mathauta (0.515 ± 0.367 mg kg^{-1}).

Table 4.5: Mean length (cm) ± standard deviation and mean Weight (g) ± standard deviation of fish species sampled at Masinga reservoir between January 2013 and December 2013.

Site	Fish Species	N	Mean Length (cm) ± StDev	Mean Weight (g) ± StDev
Kathini	Tilapia	30	19.35 ± 4.37	174.14 ± 84.79
	African Catfish	30	36.10 ± 6.13	432.23 ± 187.00
	Common Carp	31	32.87 ± 6.48	536.99 ± 312.61
Mathauta	Tilapia	32	21.42 ± 2.45	205.57 ± 56.43
	African Catfish	34	37.71 ± 8.99	455.60 ± 258.66
	Common Carp	33	33.59 ± 3.92	567.27 ± 224.44
Manyatta	Tilapia	32	22.25 ± 3.98	235.74 ± 121.85
	African Catfish	35	39.50 ± 12.10	626.40 ± 687.03
	Common Carp	36	34.95 ± 4.95	581.05 ± 231.78
Riakanau	Tilapia	33	16.91 ± 3.33	130.04 ± 86.19
	African Catfish	34	36.80 ± 8.70	483.32 ± 411.02
	Common Carp	32	28.91 ± 6.32	374.03 ± 264.17
Tumutumu	Tilapia	30	15.85 ± 3.19	94.18 ± 46.38
	African Catfish	31	34.45 ± 7.26	366.53 ± 196.13
	Common Carp	33	32.58 ± 3.56	518.87 ± 159.95

Table 4.6: Mean ± standard deviation and range values for heavy metal concentrations in muscles of Common Carp during the study period. Means in same row with different superscripts are significantly different at $p < 0.05$ levels. ND – Below detectable limit

Element/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
Cu (mg kg^{-1})	1.422 ± 1.299^{a}	1.087 ± 1.486^{a}	0.519 ± 0.426^{a}	1.054 ± 1.063^{a}	0.675 ± 0.625^{a}
Range	0.10 – 3.47	0.37 – 2.67	Nd – 0.93	0.48 – 2.17	0.25 – 1.30
Zn (mg kg^{-1})	47.649 ± 15.246^{ab}	44.424 ± 8.547^{a}	39.466 ± 14.164^{a}	62.233 ± 14.591^{b}	48.727 ± 18.079^{ab}
Range	21.91 – 74.63	29.97 – 59.43	20.94 – 62.33	51.15 – 84.73	36.30 – 72.63
Pb (mg kg^{-1})	1.424 ± 0.861^{a}	1.078 ± 0.465^{a}	1.250 ± 0.648^{a}	1.197 ± 0.463^{a}	0.994 ± 0.337^{a}
Range	0.67 – 3.28	0.44 – 1.82	0.91 – 1.68	0.13 – 1.58	0.30 – 1.48
Cr (mg kg^{-1})	0.690 ± 0.340^{a}	0.670 ± 0.656^{a}	0.709 ± 0.708^{a}	0.607 ± 0.696^{a}	0.324 ± 0.352^{a}
Range	0.08 – 1.15	0.13 – 1.28	0.25 – 1.16	0.34 -1.24	Nd – 0.88
Mn (mg kg^{-1})	0.660 ± 0.352^{a}	0.769 ± 0.246^{a}	0.783 ± 0.327^{a}	0.659 ± 0.296^{a}	1.432 ± 0.711^{b}
Range	0.12 – 1.03	0.35 – 1.14	0.24 – 1.13	0.27 – 1.28	0.55 – 2.00
Cd (mg kg^{-1})	ND	ND	ND	ND	ND

One way ANOVA revealed that there was no significant variations ($p = 0.395$; $df = 55$) in mean Cu levels observed in Tilapia muscles at the different sampling sites (Figure 4.6). The monthly variations in Cu concentration levels recorded in Tilapia fish are shown in Appendix X. The highest monthly Cu level observed in Tilapia muscles was 1.40 mg kg^{-1} at Manyatta.

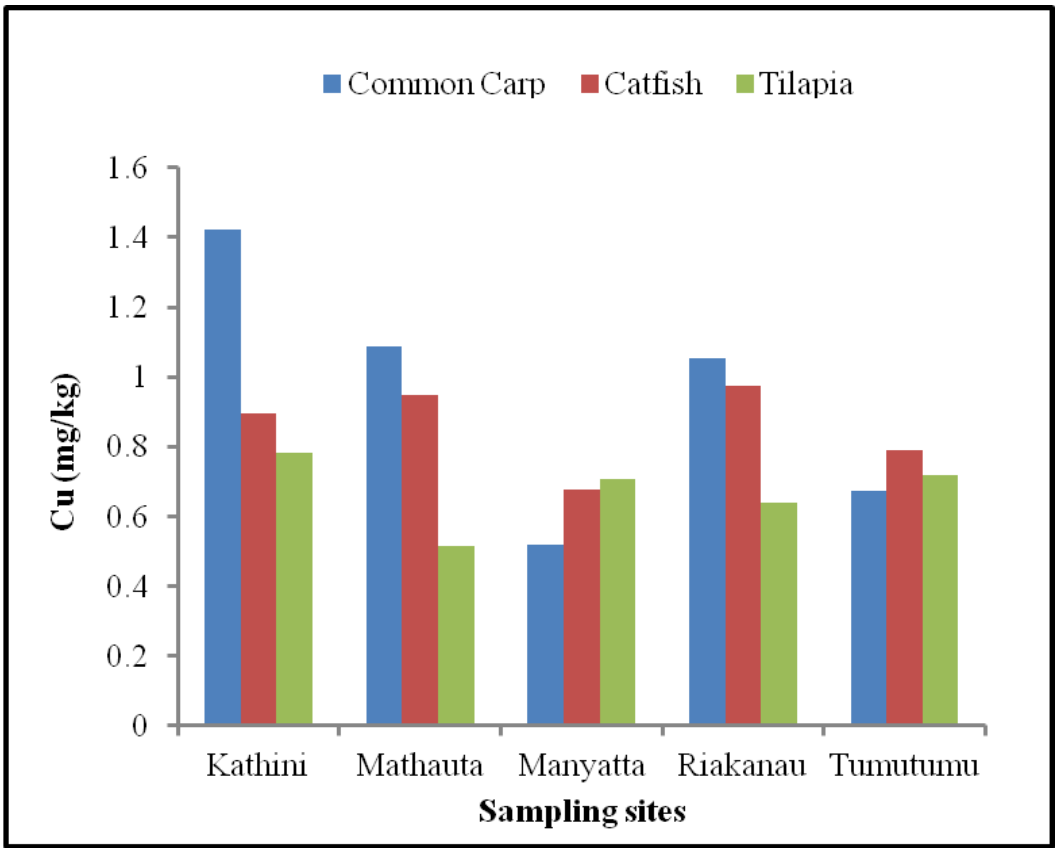

Figure 4.6: Mean Cu (mg kg^{-1}) levels in Common Carp, African Catfish and Tilapia muscles recorded between January and December, 2013 in Masinga reservoir.

The uptake of heavy metals by fish occurs from water, food and sediment. Heavy metal concentrations in the tissue of fresh water fish varies due to differences in metal concentrations and chemical characteristics of water from which fish are

sampled, their ecological needs; metabolism and feeding habits (Yilmaz, 2009). In this study, the mean Cu levels recorded at Masinga reservoir varied with fish species. Common Carp had higher Cu levels in the muscles followed by African catfish and Tilapia (Figure 4.6). The variations in Cu levels could be attributed to differences in feeding habits of the fish species. Common Carp is a bottom dweller and feeds at the bottom while Tilapia feeds from the water surface. Common carp can eat a vegetarian diet of water plants, but prefers to scavenge the bottom for insects, crustaceans including zooplankton and benthic worms (Yousafzai *et al*., 2012). This feeding behavior of Common Carp could be attributed to the slightly higher levels of Cu in the muscles. African catfish is omnivorous and preys on small fish of other species that could have led to high Cu levels as compared to tilapia which feeds on phytoplankton.

The mean Cu concentrations in fish from Masinga reservoir compared well with mean Cu concentrations in the flesh of Common Carp (1.40 mg kg^{-1}) and in Tilapia fish (0.85 mg kg^{-1}) from Lake Hashenge in Ethiopia (Asgedom *et al*., 2012). However, they were higher than mean Cu values of 0.045 mg kg^{-1} recorded in muscles tissues of tilapia fish from Tono irrigation reservoir in Ghana (Anim-Gyampo *et al.,* 2013) and lower than 2.8 – 48.84 mg kg^{-1} observed in tilapia (*Oreochromis niloticus*) of Northern delta lakes, Egypt (Saeed and Shaker, 2008).

The Cu levels in Catfish muscles obtained in Masinga reservoir were lower than Cu levels recorded in same fish species from Rasalganj fish market (15.0 ± 1.09

mg kg^{-1}) in India (Javed and Usmani, 2011) and 1.01 – 5.48 mg kg^{-1} observed in catfish muscles from River Nile, Egypt (Osman and Kloas, 2010). Studies carried out by Anim *et al.,* (2011) at Nsawam in Densu River, Ghana found very high mean Cu levels in African catfish (45.60 ± 0.74 mg kg^{-1}) and *Tilapia zilli* (91.08 ± 1.04 mg kg^{-1}). Also, mean Cu values of 1.33 ± 0.06 mg kg^{-1} have been observed in sampled *Tilapia zilli* from freshwater ecosystem at Afikpo, Nigeria (Nwani *et al.,* 2010). Oztiirk *et al.,* (2009) recorded mean Cu levels of 3.88 ± 2.18 mg kg^{-1} in muscles of Common Carp (*Cyprinus carpio*) fished from Avsar dam Lake in Turkey which was higher compared to mean Cu levels established in this study. The Cu concentration levels recorded in muscles of the three selected fish species were below the recommended limit of 3.0 mg kg^{-1} in fish and fish products (WHO, 2004).

4.5.2 Zinc (Zn) Concentration (mg kg^{-1} Dry Weight)

The mean Zn concentrations in Common Carp muscles ranged from 39.466 ± 14.164 mg kg^{-1} in Manyatta to 62.233 ± 14.591 mg kg^{-1} in Riakanau (Table 4.6). Mean Zn levels recorded at Kathini was 47.649 ± 15.246 mg kg^{-1} and Mathuata 44.424 ± 8.547 mg kg^{-1} while Tumutumu had 48.727 ± 18.079 mg kg^{-1}. There was significant difference in Zn concentration levels between the various sites ($p = 0.006$; $df = 55$). Tukey's HSD test revealed that Riakanau had Zn levels that significantly varied from Zn levels recorded at Mathauta and Manyatta. The monthly Zn level variations in Common Carp muscles are presented in Appendix XI.

Table 4.7: Mean ± standard deviation and range values for heavy metal concentrations in African Catfish during the study period. Means in same row with different superscripts are significantly different at $p < 0.05$ levels. ND – Below detectable limit

Element/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
Cu (mg kg^{-1})	0.896±0.868[a]	0.949 ±0.697[a]	0.677±0.465[a]	0.974±1.284[a]	0.791 ±0.855[a]
Range	0.28 – 2.48	0.26 – 1.95	0.20 – 1.73	0.33 – 2.30	0.23 – 2.04
Zn (mg kg^{-1})	33.999±8.685[a]	33.070±16.072[a]	37.205±12.414[a]	38.396±19.892[a]	32.929±18.279[a]
Range	21.34 – 53.00	20.96 – 55.00	23.90 – 57.00	27.63 – 59.50	17.06 – 61.00
Pb (mg kg^{-1})	0.643±0.253[a]	0.864±0.314[a]	1.057±0.494[b]	0.963±0.309[a]	1.078±0.353[b]
Range	0.48 – 1.00	0.44 – 1.56	0.54 – 1.92	0.58 – 1.47	0.28 – 1.56
Cr (mg kg^{-1})	0.848±0.460[a]	0.858±0.459[a]	0.760±0.233[a]	0.791±0.586[a]	0.566±0.233[a]
Range	0.40 – 1.56	0.20 – 1.65	0.26 -1.11	0.50 – 1.23	0.20 – 1.05
Mn (mg kg^{-1})	0.452±0.368[a]	0.525±0.671[a]	0.777±0.737[a]	0.485±0.269[a]	0.990±0.984[a]
Range	0.08 – 1.00	0.19 – 1.05	0.35 – 1.13	0.10 – 0.79	0.10 – 1.66
Cd (mg kg^{-1})	ND	ND	ND	ND	ND

The mean Zn concentration levels in African Catfish muscles varied (Table 4.7) with the highest levels observed at Riakanau (38.396 ± 19.892 mg kg^{-1}) and the lowest at Tumutumu (32.929 ± 18.278 mg kg^{-1}). Kathini and Mathauta had mean Zn concentrations of 33.999 ± 8.685 mg kg^{-1} and 33.070 ± 16.072 mg kg^{-1} respectively. Manyatta recorded a mean Zn level of 37.205 ± 12.414 mg kg^{-1}. One way ANOVA revealed no significant difference ($p = 0.869$; $df = 55$) between the sampling sites (Figure 4.7). The monthly variations of Zn concentration levels in each sampling sites are showed in Appendix XII.

The mean values for Zn concentrations in tilapia showed modest variations (Table 4.8). The concentrations recorded were 29.645 ± 5.302 mg kg^{-1} (Kathini), 33.177± 10.562 mg kg^{-1} (Manyatta), 37.258 ± 9.843 mg kg^{-1} (Riakanau) and 35.714 ± 9.580 mg kg^{-1} (Tumutumu) and 37.999 ± 9.692 mg kg^{-1} (Mathauta). One way ANOVA showed no significant differences ($p = 0.176$; $df = 55$) in mean Zn concentration levels between different sites (Figure 4.7). The monthly variations in Zn concentration levels in Tilapia muscles are indicated in Appendix XIII.

The main source of Zn pollution in aquatic environment is from fertilizers, sewage sludge, industrial wastes and mining (Bradi, 2005). Therefore, the source of Zn in the study area could be attributed to use of inorganic fertilizers within Masinga reservoir catchment. Also, Zn could be from sewage sludge from the towns distributed within the catchment such as Thika, Murang'a, Maragua, Sagana and Karatina to mention a few. The elevated Zn levels observed at Riakanau may be

due to upcoming irrigation farms within Masinga reservoir. These farms use a lot of fertilizers during the dry seasons for growing horticultural crops.

The variations in heavy metal concentrations in freshwater fish is attributed to differences in metal concentrations in water, feeding patterns of fish and the season in which studies are done (Canli *et al.*, 1998). The mean Zn concentration levels recorded in the African catfish and Tilapia showed modest variations in all the sampling sites (Figure 4.7). However, Common Carp had higher mean Zn levels in all sampling sites. Common carp feeds from the bottom, where it grubs through bottom sediments for food. Heavy metal contamination in sediments is known to affect water quality and also leads to bioaccumulation of metals in aquatic organisms (Fernandes *et al.,* 2007). In this study, the sediments of Masinga reservoir showed high Zn concentration levels, hence the high Zn levels in Common Carp muscle tissues unlike the other fish species.

Compared to mean Zn concentration levels recorded in similar fish species from other aquatic ecosystems, slightly higher levels (11.62 – 71.85 mg kg^{-1}) in African Catfish muscles have been recorded in River Nile, Egypt (Osman and Kloas, 2010). Anim-Gyampo *et al.,* (2013) obtained lower mean Zn levels (0.004 mg kg^{-1}) in tilapia caught from Tono irrigation reservoir in Ghana. Studies carried out in Lake Hashenge, Ethiopia revealed comparable Zn levels in Tilapia (24.95 ± 1.80 mg kg^{-1}) and Common carp (46.08 ± 1.93 mg kg^{-1}) muscles (Asgedom *et al.*, 2012).

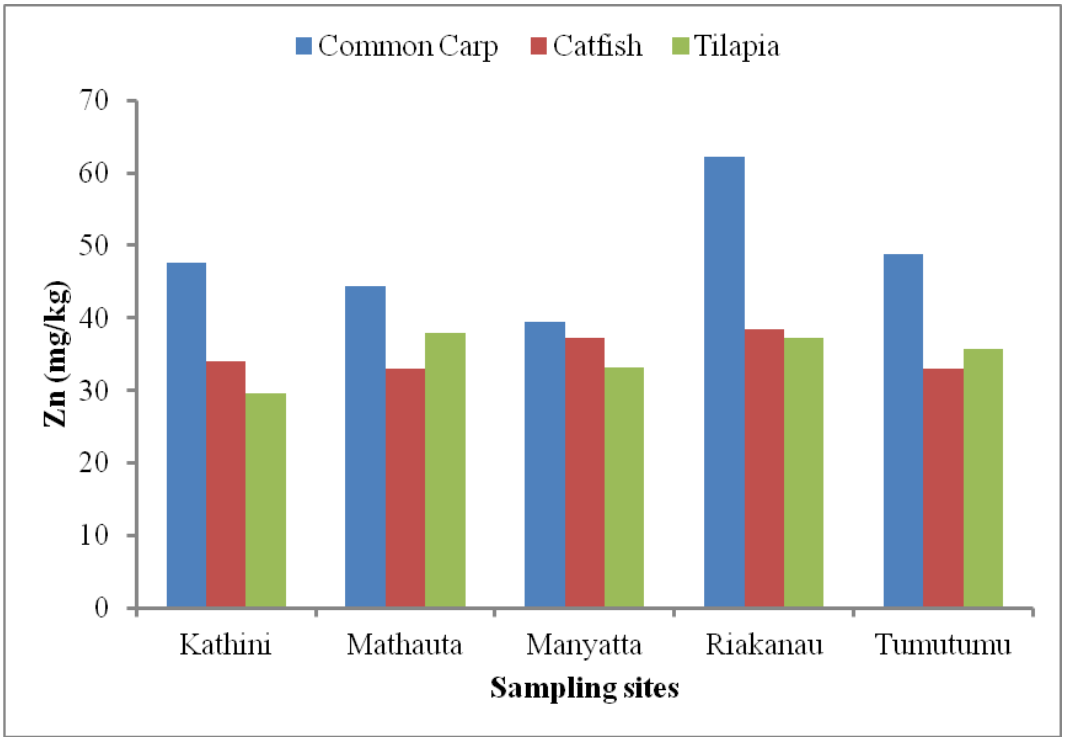

Figure 4.7: Mean Zn (mg kg^{-1}) levels in Common Carp, African Catfish and Tilapia muscles recorded between January and December, 2013 in Masinga reservoir.

The Zn concentration levels recorded in Tilapia fish in Masinga reservoir were also lower than 28.00 – 76.33 mg kg^{-1} obtained in Athi river system (Muiruri *et at.*, 2013). Anim *et al.,(*2011) observed lower mean Zn levels in African Catfish muscles (19.84 ± 0.16 mg kg^{-1}) and but comparable levels in *Tilapia zilli* (28.24 ± 0.84 mg kg^{-1}) sampled from Densu River, Ghana. Mean Zn levels recorded by Kumar *et al.*, (2011) in Tilapia (*Oreochromis niloticus*) muscle tissues (51.20 ±3.90 mg kg^{-1}) obtained from aquaculture ponds in Kolkata wetlands, India was higher than levels observed in this study. In Afikpo freshwater ecosystem in Nigeria, lower mean Zn levels in *Tilapia zilli* have been observed (Nwani *et al.*,

2010). The mean Zn levels recorded during this study in the three food fish species were below the 75 mg kg^{-1} recommended limit for Zn in fish and fish products (FAO, 2003).

4.5.3 Lead (Pb) Concentration (mg kg^{-1} Dry Weight)

The Pb mean levels recorded in common carp muscles during the study showed modest variations (Table 4.6). The lowest Pb mean level was 0.994 ± 0.337 mg kg^{-1} (Tumutumu) and the highest 1.424 ± 0.861mg kg^{-1} (Kathini) as shown in Figure 4.8. Mathauta, Manyatta and Riakanau recorded 1.078 ± 0.465 mg kg^{-1}, 1.250 ± 0.648 mg kg^{-1} and 1.197 ± 0.463 mg kg^{-1} respectively. One way ANOVA showed no significant difference between the sampling stations ($p = 0.435$; $df = 55$). The monthly variations in Pb levels in Common Carp muscles are presented in appendix XIV.

The mean Pb concentration levels recorded in African Catfish are shown in Table 4.7. Tumutumu recorded the highest mean Pb levels (1.078 ± 0.353 mg kg^{-1}), followed by Manyatta (1.057 ± 0.494 mg kg^{-1}). The lowest mean Pb concentration levels in Catfish were observed at Kathini (0.643 ± 0.253 mg kg^{-1}), while Mathauta and Riakanau recorded 0.864 ± 0.314 mg kg^{-1} and 0.963 ± 0.309 mg kg^{-1} respectively. The results exhibited significance difference in Pb concentration levels recorded at different sampling sites ($p = 0.026$; $df = 55$). Tukey's HSD test showed that Pb levels in Catfish from Tumutumu and Manyatta were significantly different from levels recorded in the other sampling sites (Figure 4.8).

Table 4.8 Mean ± standard deviation and range values for heavy metal concentrations in Tilapia during the study period. Means in same row with different superscripts are significantly different at $p < 0.05$ levels. ND – Below detectable limit

Element/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
Cu (mg kg^{-1})	0.782±0.327[a]	0.515±0.367[a]	0.709±0.352[a]	0.640±0.309[a]	0.717±0.366[a]
Range	0.34 – 1.18	0.10 – 1.31	0.13 – 1.40	0.20 – 1.30	0.11- 1.25
Zn (mg kg^{-1})	29.645±5.302[a]	37.999±9.692[a]	33.177±10.562[a]	37.258±9.843[a]	35.714±9.580[a]
Range	25.50 – 41.90	24.00 – 57.50	18.69 – 54.33	21.95 – 55.90	17.50 – 54.63
Pb (mg kg^{-1})	0.765±0.413[a]	0.684±0.315[a]	0.609±0.353[a]	0.650±0.228[a]	0.552±0.404[a]
Range	0.21 – 1.57	0.25 – 1.31	Nd – 1.07	0.32 – 1.03	Nd – 1.08
Cr (mg kg^{-1})	0.559±0.222[a]	0.679±0.315[a]	0.791±0.402[a]	0.541±0.304[a]	0.652±0.521[a]
Range	0.20 – 0.85	0.41 – 1.23	0.40 – 1.15	0.16 – 1.00	0.43 – 1.02
Mn (mg kg^{-1})	0.518±0.303[a]	0.183±0.290[a]	0.217±0.377[a]	0.409±0.414[a]	1.480±0.312[b]
Range	0.23 – 0.90	Nd – 0.74	Nd – 0.96	0.16 – 1.00	0.96 – 1.78
Cd (mg kg^{-1})	ND	ND	ND	ND	ND

Appendix XV shows the monthly variations of Pb concentration levels in Catfish muscles as observed in the study.

Mean Pb concentration levels found in Tilapia muscles exhibited very little variations and are recorded in Table 4.8. The mean concentrations ranged from 0.552 ± 0.404 mg kg^{-1} at Tumutumu to 0.765 ± 0.413 mg kg^{-1} at Kathini. Mathauta and Manyatta had 0.684 ± 0.315 mg kg^{-1} and 0.609 ± 0.353 mg kg^{-1} respectively. Mean Pb concentration recorded at Raiakanau was 0.650 ± 0.288 mg kg^{-1}. One way ANOVA established no significant difference ($p = 0.645$; $df = 55$) in Pb concentration levels recorded in tilapia muscles between the sampling stations (Figure 4.8). The temporal variations in Pb concentration levels recorded during the study are indicated in Appendix XVI. The results showed moderate monthly variations of Pb levels in the Tilapia muscles.

The high mean Pb levels observed at Kathini for both Common Carp and Tilapia and at Tumutumu for Catfish could be attributed to the elevated levels recorded in sediments and surface water. Fish obtain heavy metals from water, sediments or through the food chain. Common carp had higher Pb levels compared to African Catfish while Tilapia had the lowest Pb levels in the muscle tissues. The mean Pb concentration levels recorded in the three fish species during this study were lower than the WHO recommended limit of 2.0 mg kg^{-1} for Pb in fish and fish products (WHO, 2004).

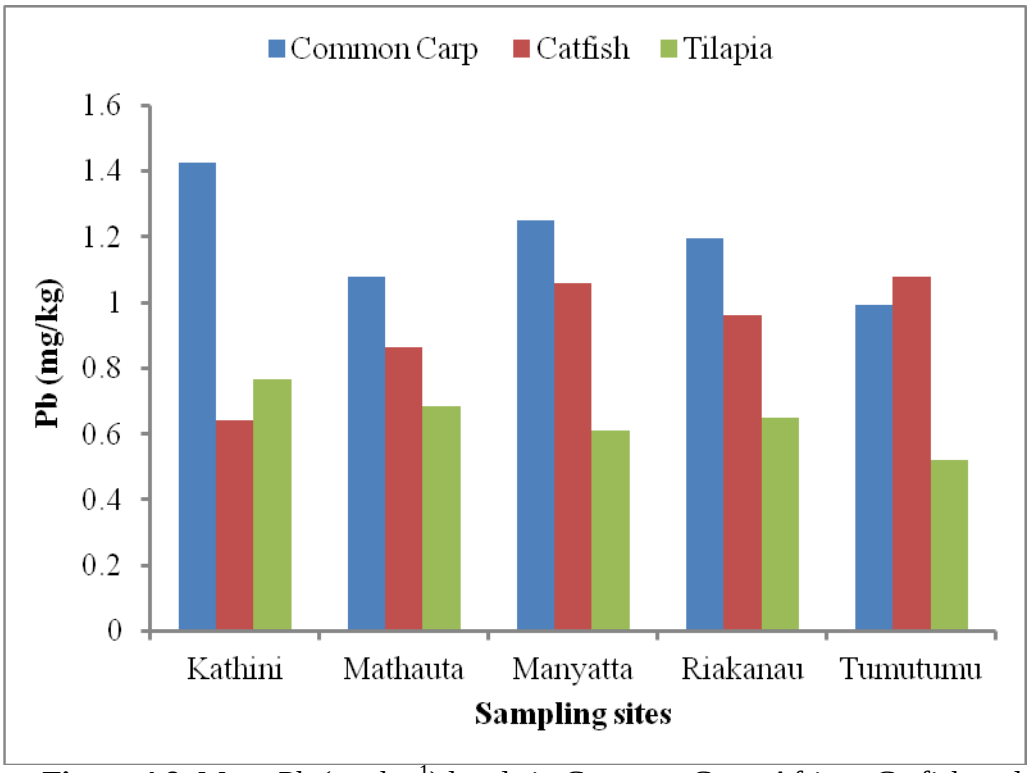

Figure 4.8: Mean Pb (mg kg^{-1}) levels in Common Carp, African Catfish and Tilapia muscles recorded between January and December, 2013 in Masinga reservoir

The Pb concentration recorded in Common carp muscles at Masinga reservoir is comparable to levels obtained in Common Carp muscles (1.24± 0.20 mg kg^{-1}) from Lake Hashenge, Ethiopia (Asgedom *et al.*, 2012). In this study lower Pb levels were obtained compared to results observed in African Cafish in Lake Victoria (Tole and Shitsama, 2003) and 5.895 – 14.51 mg kg^{-1} in River Nile, Egypt (Osman and Kloas, 2010). In Avsar dam Lake in Turkey, higher mean Pb (2.14 ± 2.09 mg kg^{-1}) in Common Carp (*Cyprinus carpio*) muscles have been recorded (Oztiirk *et al.*, 2009). Anim *et al.*, (2011) recorded much lower mean Pb levels in African Catfish muscles (0.08 ± 0.01 mg kg^{-1}) and *Tilapia zilli* (0.34 ±

0.02 mg kg^{-1}) from Densu River, Ghana. Studies done by Nwani *et al.,* (2010) observed lower mean Pb levels (0.31 ± 0.01 mg kg^{-1}) in *Tilapia zilli* from Afikpo freshwater ecosystem in Ghana.

4.5.4 Chromium (Cr) Concentration (mg kg^{-1} Dry Weight)

Mean Cr concentration levels in Common Carp muscles are shown in Table 4.6. The highest mean Cr levels were recorded in Manyatta (0.709 ± 0.708 mg kg^{-1}), followed by Kathini (0.690 ± 0.340 mg kg^{-1}). Tumutumu recorded the lowest Mean Cr levels of 0.324 ± 0.352 mg kg^{-1}, while Mathauta and Riakanau had 0.670 ± 0.656 mg kg^{-1} and 0.607 ± 0.696 mg kg^{-1} respectively. This study revealed no significant differences ($p = 0.456$; $df = 55$) in mean Cr concentration levels in the muscles of Common carp from the five sampling stations (Table 4.6 and Figure 4.9). The temporal variations in Cr concentration levels recorded in Common Carp muscles are shown in Appendix XVII.

The mean Cr concentration levels recorded in African Catfish at different sites are shown in Table 4.7. The concentrations ranged from 0.566 ± 0.233 mg kg^{-1} (Tumutumu) to 0.858 ± 0.459 mg kg^{-1} (Mathauta). The mean Cr levels observed at Kathini, Manyatta and Raiakanu was 0.848 ± 0.460 mg kg^{-1}, 0.760 ± 0.233 mg kg^{-1} and 0.791 ± 0.586 mg kg^{-1} respectively. One way ANOVA established no significant difference ($P = 0.180$; $df = 55$) between the sites (Figure 4.9). The monthly Cr levels observed in African Catfish muscles are indicated in Appendix XVIII.

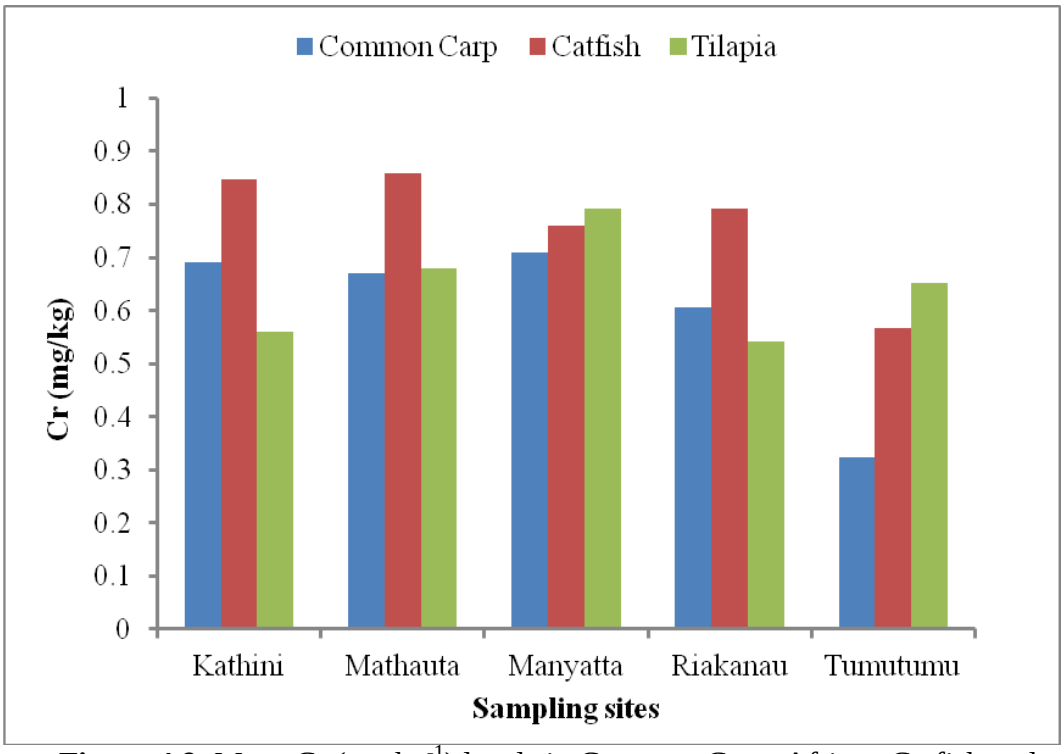

Figure 4.9: Mean Cr (mg kg^{-1}) levels in Common Carp, African Catfish and Tilapia muscles recorded between January and December, 2013 in Masinga reservoir

The Cr concentration levels observed in Tilapia muscles are presented in Table 4.8. The levels ranged from 0.541± 0.304 mg kg^{-1} (Riakanau) to 0.791 ± 0.402 mg kg^{-1} (Manyatta) (Figure 4.9). Other mean Cr levels recorded in tilapia muscle tissues were 0.559 ± 0.222 mg kg^{-1}, 0.679 ± 0.315 mg kg^{-1} and 0.652 ± 0.521mg kg^{-1} for Kathini, Mathauta and Tumutumu respectively. Appendix XIX shows the monthly Cu levels recorded during the study at different sampling sites. One way ANOVA revealed that there was no significant difference ($p = 0.464$; $df = 55$) in mean Cr levels observed in Tilapia muscles in the sampling sites.

The mean Cr concentration levels recorded in the three fish species from Masinga reservoir were higher than recommended limit of 0.15mg/kg chromium in fish and fish products (WHO, 2008). The higher concentrations observed in the fish species could be attributed to high levels of Cr recorded in sediments of Masinga reservoir.

The mean Cr concentration recorded in Masinga reservoir was similar to 0.65 ± 0.14 mg kg^{-1} found in Common Carp and higher than 0.37 ± 0.14 mg kg^{-1} in Tilapia *Oreochromis niloticus* muscles sampled from Hashenge Lake, Ethiopia (Asgedom *et al.,* 2012). Also, the Cr levels were within same range as 0.05 – 0.9 mg kg^{-1} in *Clarias gariepinus* muscles from River Nile, Egypt (Ibrahim and Omar, 2013).). Ugwu *et al.,* (2012) observed comparable Cr levels (0.56 mg kg^{-1}) in muscles of Tilapia *Oreochromis niloticus* obtained from river Usuma, Nigeria. However, mean Cr levels obtained in this study were lower compared to 2.37 – 5.47 mg kg^{-1} in African Catfish muscles sampled from River Nile (Osman and Kloas, 2010) and 1.19 ± 0.31 mg kg^{-1} recorded in Common Carp muscles from Lake Mogan, Turkey (Benzer *et al.,* 2013). *Cyprinus carpio* sampled from Avsar dam Lake was found to have higher mean Cr levels (1.18 ± 0.73 mg kg^{-1}) in the muscles (Oztiirk *et al.,* 2009) in comparison to values got in Masinga reservoir.

4.5.5 Manganese (Mn) Concentration (mg kg^{-1} Dry Weight)

The lowest mean Mn concentration level in common Carp muscles was 0.659 ± 0.296 mg kg^{-1} (Riakanau) while the highest was 1.432 ± 0.711 mg kg^{-1}

(Tumutumu) as indicated in Table 4.6. Other recorded mean Mn levels in Common Carp muscles were 0.769 ± 0.246 mg kg^{-1} (Mathauta), 0.783 ± 0.327 mg kg^{-1} (Manyatta) and 0.660 ± 0.352 mg kg^{-1} (Kathini). One way ANOVA showed that there were significantly differences ($p = 0.001$; $df = 40$) in Mn levels measured at different sampling sites (Figure 4.10). Tukey's HSD test revealed that mean Mn levels recorded at Tumutumu in Common Carp muscles was significantly different from the Mn levels observed in the other sampling sites.

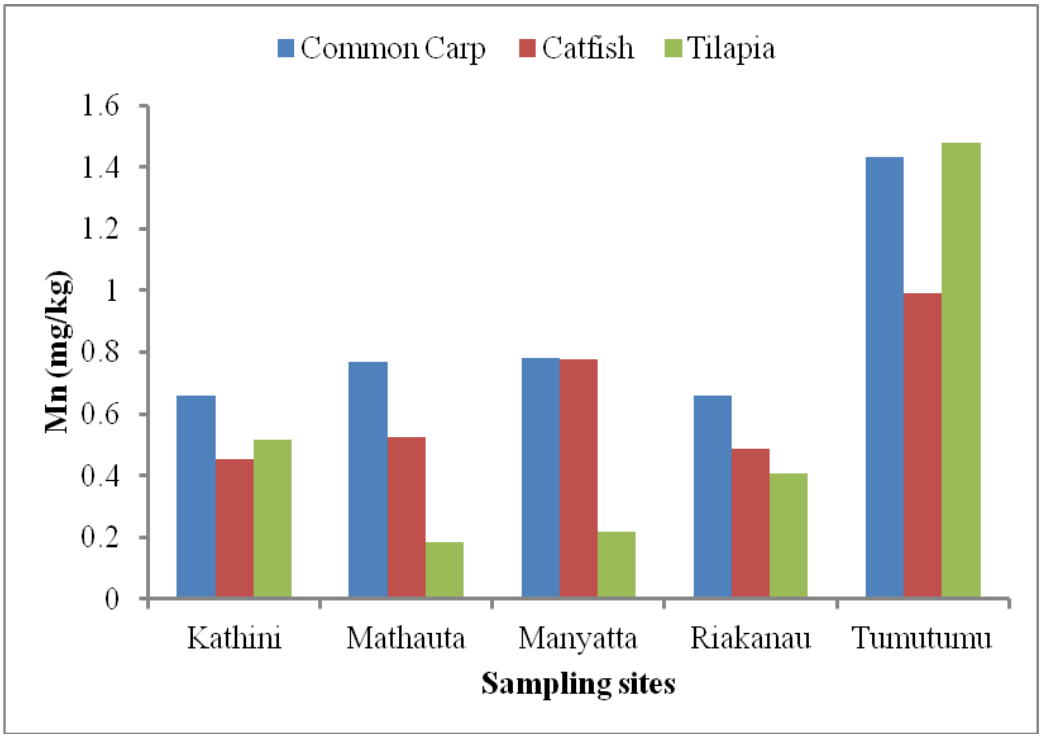

Figure 4.10: Mean Mn (mg kg^{-1}) levels in Common Carp, African Catfish and Tilapia muscles recorded between January and December 2013 in Masinga reservoir.

Mean Mn concentration levels recorded in African Catfish from different sampling sites is shown in Table 4.7. The highest levels were observed at Tumutumu (0.990 ± 0.984 mg kg^{-1}) followed by Manyatta (0.777 ± 0.737 mg kg^{-1} and the lowest levels (0.452±0.368 mg kg^{-1}) at Kathini (Figure 4.10). Mathauta and Riakanau had mean Mn levels of 0.525 ± 0.671 mg kg^{-1} and 0.485 ± 0.269 mg kg^{-1} respectively. One way ANOVA showed that there was no significant difference ($p = 0.575$; $df = 55$) in Mn Concentration levels in Catfish between the sampling sites (Figure 4.10).

The mean Mn concentration levels obtained in Tilapia muscles are shown in Table 4.8. The levels ranged from 0.183 ±0.290 mg kg^{-1} (Mathauta) to 1.480 ± 0.312 mg kg^{-1} (Tumutumu). Mean Mn concentration levels observed in other sampling sites were 0.518 ± 0.303 mg kg^{-1} (Kathini), 0.217 ± 0.377mg kg^{-1}(Manyatta) and 0.409 ± 0.414 mg kg^{-1} (Riakanau). One way ANOVA showed significance difference ($p= 0.00$; $df = 25$) in Mn levels obtained at different sampling sites. Tukey's HSD test revealed that Mn concentration levels observed at Tumutumu (1.480 ± 0.312 mg kg^{-1}) significantly varied from the rest of the sampling sites.

The high mean Mn concentration levels for the three different fish species observed in Tumutumu, could be attributed to the high Mn levels recorded in surface water at the same sampling site during this study. Mn is one of the commonly found elements in the lithosphere. It is an essential micro nutrient and functions as a co factor for many enzyme activities (Suresh *et al.,* 1999).

However, high Mn concentration interferes with central nervous system of invertebrates and hence a matter of concern as the consumption of Mn contaminated fish could result to Mn related disorders in the consumers (Krishna *et al.*, 2014). The Mn concentration levels obtained in the three fish species during this study did not exceed the WHO recorded limit of 2.50 mg/kg for fish and fish products (FAO/WHO, 1984).

Mean Mn concentration recorded in this study were lower comapared to mean Mn levels in muscles of *Cyprinus carpio* (1.79 ± 0.53 mg kg^{-1}) and Tilapia *Oreochromis niloticus* (1.01 ± 0.32 mg kg^{-1}) sampled from Hashenge Lake, Ethiopia (Asgedom *et al.*, 2012). Also, lower compared to 1.00 ± 0.24 mg kg^{-1} in muscles of *Cyprinus carpio* fished from Lake Mogan, Turkey (Benzer *et al.*, 2013), 1.74 mg kg^{-1} in Tilapia from Densu river, Ghana (Makimilua and Afua, 2013) and 1.18 mg kg^{-1} in *Tilapia zilli* sampled from River Benue, Nigeria (Eneji *et al.*, 2011). However, the concentrations compared well with Mn levels 0.78 mg kg^{-1} and 0.607 mg kg^{-1} in muscles of *Clarias gariepinus* from Densu River, Ghana (Makimilua and Afua, 2013) and River Benue, Nigeria (Eneji *et al.*, 2011) respectively.

4.6 Relationships of Heavy Metal Concentrations in Water, Sediments and Three Fish Species

4.6.1 Correlation Analysis of Heavy Metals in Water, Sediments and Fish

Pearson correlation coefficients calculated to obtain associations between heavy metal variables in surface water, sediments and the three fish species are shown in Tables 4.9 and 4.10. The Concentration of Cu in surface water showed a positively significant correlation with Cu levels in sediments ($r = 0.405$; $p = 0.027$) and Pb levels in sediments ($r = 0.463$; $p = 0.010$). The Pb levels in surface water had a significant correlations with Cu levels in Common Carp muscles ($r = 0.442$; $p = 0.015$), Mn levels in Common Carp muscles ($r = 0.414$; $p = 0.023$) and Mn levels in Catfish muscles ($r = 0.429$; $p = 0.018$).

Chromium levels in surface water revealed a positively significant correlation with Cu levels in Tilapia muscles ($r = 0.490$; $p = 0.006$), Zn levels in tilapia muscles ($r = 0.564$; $p = 0.001$) and Pb levels in tilapia muscles ($r = 0.394$; $p = 0.031$). The Cr levels in surface water had also a significant correlation with Mn levels in sediments ($r = 0.366$; $p = 0.046$). The study showed a significant correlation between Mn levels in surface water and Mn levels in Tilapia muscles ($r = 0.620$; $p = 0.000$). The Mn levels in surface water had also a positively significant correlation with Pb levels in Catfish muscles ($r = 0.435$; $p = 0.016$). Zn levels in water had a negatively significant correlation with Mn levels in sediments ($r = -0.568$; $p = 0.001$).

Table 4.9: Pearson Correlation matrix for heavy metals in sediments and surface water. *Correlation is significant at p<0.05 level (2-tailed)

	Cu Sediments	**Zn Sediments**	**Pb Sediments**	**Cr Sediments**	**Mn Sediments**	**Cu Water**	**Zn water**	**Pb water**	**Cr water**	**Mn Water**
Cu - Sediments	1.000									
Zn - Sediments	**.601***	1.000								
Pb - Sediments	.324	.194	1.000							
Cr - Sediments	.338	**.383***	.291	1.000						
Mn - Sediments	.266	.015	.038	.156	1.000					
Cu - Water	**.405***	.153	**.463***	.054	.070	1.000				
Zn - water	-.044	.346	-.022	.032	**-.568***	.100	1.000			
Pb - water	.043	-.260	-.167	.084	-.100	-.290	-.081	1.000		
Cr - water	.267	.194	-.029	.039	**.366***	.338	-.092	.203	1.000	
Mn - Water	-.131	-.329	-.221	.113	-.054	-.146	-.102	.159	-.0700	1.000

Table 4.10: Pearson Correlation matrix for heavy metal levels in sediments, surface water and different fish species. *Correlation is significant at p<0.05 level (2-tailed)

	Cu Sediments	**Zn - Sediments**	**Pb - sediments**	**Cr- Sediments**	**Mn - Sediments**	**Cu - Water**	**Zn water**	**Pb - water**	**Cr - water**	**Mn - Water**
Cu Carp	-.213	-.141	.116	.038	-.019	-.106	-.006	**.442***	-.130	.079
Zn Carp	.036	-.114	-.063	.233	.089	.106	.134	-.019	.234	.337
Pb- Carp	-.041	-.020	-.100	.111	.117	-.081	-.082	.155	.026	-.018
Cr -carp	-.166	-.055	-.232	.012	.113	-.090	-.057	-.143	.153	-.073
Mn carp	-.068	-.085	-.293	-.248	-.144	-.253	.060	**.414***	.121	-.022
Cu Catfish	-.112	-.068	-.036	-.241	-.081	-.107	-.250	-.231	-.139	-.043
Zn Catfish	-.214	-.102	-.215	-.275	.025	-.357	-.057	-.033	-.033	-.015
Pb - Catfish	.263	-.018	-.141	-.030	.177	-.168	-.069	.247	.271	**.435***
Cr - catfish	.067	.028	-.229	-.005	.039	.003	-.089	-.045	.026	-.042
Mn catfish	-.217	-.345	-.241	-.275	-.284	-.238	.084	**.429***	-.171	.035
Cu -Tilapia	.088	.006	**-.406***	.249	**.393***	-.059	-.072	.292	**.490***	.274
Zn - Tilapia	**.391***	.036	-.060	-.028	.213	.285	-.038	.144	**.564***	-.069
Pb - tilapia	-.124	.061	-.002	-.114	.117	-.013	-.012	.052	**.394***	.099
Cr - Tilapia	-.083	-.288	-.154	-.094	.183	-.132	-.230	.192	-.040	.071
Mn Tilapia	-.139	-.275	-.323	-.079	.078	-.221	.069	.129	-.096	**.620***

Copper levels in sediments had a significant correlation with Zn levels in tilapia muscles (r = 391; p = 0.033) and Zn in sediments (r = 0.601; p = 0.000). Manganese in sediments had a weak positive correlations with Cu levels in Tilapia muscles (r = 0.393; p = 0.032) while Pb levels in sediments had a negative significant correlation with Cu levels in Tilapia muscles (r = -0.406; p = 0. 026). The concentration of Zn in sediments had a significant correlation with Cr levels in sediments (r = 0.383; p = 0.036).

The correlation between heavy metals is influenced by physical and chemical processes occurring in an aquatic environment (Baeyens *et al.,* 1998a). The correlations between different metals may have resulted from similar accumulation behavior of the metals in the fish species and their interactions (Rejomon *et al.,* 2010). The noted significant correlations among the heavy metals may be a reflection of a common source of occurrence and an indication of similar biogeochemical pathways for subsequent accumulation in the muscle tissues of the fish species (Kumar *et al.,* 2011).

4.6.2 Bioaccumulation Transfer Factor

The transfer factor (TF) of heavy metals in the fish species from Masinga reservoir water and sediments are presented in Table 4.11. The TF of Cu from water to the three fish species ranged from 61.964 (Tilapia) to 87.649 (Common carp) while from sediments it ranged from 0.039 to 0.055. TF of all heavy metals from sediments to the fish muscle tissues was less than 1.00 and more than 1.00

from water to fish muscle tissues and this agrees with what Asgedom *et al.*, (2012) obtained in Hashenge Lake, Ethiopia. The trends of TF for heavy metals from water to Tilapia fish muscles were in the ranking order Zn>Cr>Pb>Cu>Mn; in Catfish Zn>Pb>Cr>Cu>Mn and Zn>Pb>Cr>Cu>Mn for Common carp. Canterford *et al.*, (1978) reported that it is useful to express results of bioaccumulation in terms of TF when comparing the order of uptake of metals. TF is the ratio of a specific heavy metal in the organism (fish muscle) to the concentration of the metal in the reservoir water or sediment according to Kalfakakour and Akrida-Demertzi (2000) and Rashed (2001).

Table 4.11: Transfer Factor (TF) of heavy metals in muscle tissues of different fish species from Masinga reservoir

Fish Species	Ecosystem Component	Cu	Zn	Pb	Cr	Mn
Tilapia	Water	61.964	314.653	121.487	144.730	10.052
	Sediments	0.039	0.711	0.051	0.020	0.001
African Catfish	Water	79.021	317.922	171.628	167.392	11.284
	Sediments	0.050	0.719	0.072	0.023	0.001
Common Carp	Water	87.649	439.044	221.470	131.614	15.035
	Sediments	0.055	0.993	0.094	0.018	0.002

When fish are exposed to high levels of metals in an aquatic environment, they absorb the bio-available metals either through the gills and skin or through the

ingestion of contaminated water or food. However, the presence of metals in high levels does not indicate a direct toxic risk to fish, if there is no significant accumulation of metals by fish tissues (Kamaruzzaman *et al.,* (2010).

According to Heath (1991), metals in fish are regulated (uptake and loss system) in the fish body to a certain level beyond which bioaccumulation of metals takes place. This study showed that TF of water were greater than those of sediments. This was a sign of close correlation between heavy metal concentrations in water and fish. Therefore, it can be inferred that the major source of heavy metal contamination of fish species in Masinga Reservoir is from water. This agrees with other studies done elsewhere. For example Rashed (2001) determined TF for Cr, Cu, Zn and Mn from water and sediment in Tilapia fish from Lake Nasser, Egypt and found only TFs from water were more than 1.00. Also, Abdel-Baki *et al.*, (2011) observed similar results when they calculated TFs of heavy metals from water and sediment in Tilapia fish. Fish accumulate metals from water by diffusion through skin and gills as well as oral consumption of water (Oguzie, 2003).

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1.1 Physical Parameters

Electrical conductivity and pH were within the WHO set limits for drinking water while surface water temperature and dissolved oxygen were within acceptable limits for survival of warm water fish species in Masinga reservoir. Turbidity was above the WHO set guidelines for drinking water. Due to the high turdidity levels it was concluded that water from Masinga reservoir is not suitable for domestic use without prior treatment. Also, the turbidity levels are not suitable for hatching of fish eggs. The high turbidity level is an evidence of the poor land use practices and other anthropogenic activities within Masinga reservoir catchment.

5. 1.2 Heavy Metal Concentrations in Water and Sediments

The heavy metals studied (Cu, Zn, Pb, Cr, Cd and Mn) had lower levels than WHO recommended limit for drinking water. Therefore, it was concluded that the surface water in Masinga reservoir is fit for human consumption. The heavy metal concentrations in sediments were below WHO set limits for survival of aquatic organisms except for Cr. Tumutumu had higher levels of Cr concentrations in sediments while Kathini and Manyatta were slightly polluted with Cr. This demonstrates that there are industrial wastes that reach Masinga reservoir from the catchment activities.

5. 1.3 Heavy Metal Concentrations in Fish Species

The concentrations of Cu, Zn, Pb, and Mn in muscle tissues of *Cyprinus Carpio*, *Clarias gariepinus* and *Oreochromis spirulus niger* were below the WHO recommended limit for fish and fish products. Hence, these metals have no immediate threat on the health of consumers of fish and fish products from Masinga reservoir. However, the levels of Cr in the muscle tissues of the three fish species exceeded the WHO limits for Cr in fish and fish products. This exposes the consumers of fish and fish products from Masinga reservoir to health risks.

5. 1.4 Heavy Metals Relationships in Water, Sediments and Fish Species

The sediments of Masinga reservoir had higher levels of heavy metal contamination than in surface water and the biotic environment. However, the three fish species bioaccumulated heavy metals mostly from the water component. Generally, the heavy metal concentrations in fish muscle tissues was in the order *Cyprius carpio* > *Clarias gariepinus* > *Oreochromis spirulus niger* for all metals except for Cr which was higher in *Clarias gariepinus* compared to the other fish species. It was also observed that there were significant correlations between heavy metals in surface water, sediments and the fish species. These significant correlations of metals are an indication of a common source of pollution into the reservoir.

5.2 Recommendations

5.2.1 Management of Masinga Reservoir

Considering the current heavy metal levels in sediments, water and fish species in Masinga reservoir, this study recommends for an integrated management plan for the reservoir. This will require involvement of all stakeholders within the catchment and will go along way in curbing aquatic pollution emenating from human activities. The activities in the management plan should include regular monitoring of heavy metal contaminants in aquatic ecosystems especially in fish and fish products from Masinga reservoir. The relevant state agencies such as the State Department of Fisheries, NEMA, TARDA and WARMA should take lead in the monitoring activities.

The elevated Cr concentrations in sediments and fish species is a sign of untreated or unadequately treated wastewater most probably from tanneries located in the catchment. The wastewaters emanating from the tanning process should be properly and adeaquately treated to meet the minimum set standards before being released to the aquatic environment.

5.2.2 Further Research

The following following is recommended:-

1. Further research to find the concentrations of the heavy metals studied, in different fish organs such as gills, skin and intestines. Also, recommended

is research to find out the levels of heavy metals in sediments at different depths.

2. Research on other heavy metals not covered in this study to find out their concentration levels in sediments, water, macro-benthos and different fish species within the reservoir
3. Research on human health effects due to heavy metal bioaccumulation especially for Cr whose concentration levels in the three fish species studied was found to exceed the recommended WHO limits.
4. Finally it is recommended that a social study be carried to find out the level of public awareness on the dangers of aquatic pollution to the users of natural resources within Masinga reservoir especially water and fish.

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APPENDICES

Appendix I: Temporal variations in surface water temperature (^{0}C) at different sampling sites during the study period.

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	28.43	26.33	26.27	23.80	26.27
February	29.10	30.50	26.43	26.47	27.00
March	28.33	26.90	26.67	26.53	26.30
April	29.33	29.90	26.63	27.03	26.97
May	25.77	23.13	24.63	24.77	24.70
June	28.50	25.37	24.20	24.50	25.30
July	28.40	26.47	26.30	24.03	24.63
August	22.93	21.03	22.23	21.53	22.33
September	23.70	21.60	22.83	22.00	23.50
October	26.30	24.83	24.57	24.70	24.20
November	30.43	28.50	26.80	26.73	25.83
December	29.13	28.17	27.63	27.10	27.30

Appendix II: Temporal variations in Dissolved Oxygen (mg L^{-1}) at different sampling sites during the study period.

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	5.53	6.57	6.47	5.70	5.87
February	1.30	3.67	4.80	5.10	5.13
March	3.90	4.50	3.87	3.57	4.53
April	5.57	6.50	5.86	5.96	5.93
May	1.07	1.17	1.23	1.27	1.23
June	3.91	4.82	5.20	4.91	5.17
July	6.87	6.91	5.32	5.90	6.78
August	8.73	7.94	8.63	8.70	8.78
September	5.50	5.37	7.47	5.77	5.77
October	4.67	5.40	5.43	5.87	5.67
November	5.10	6.83	6.60	6.67	6.13
December	3.73	3.93	3.47	3.10	3.23

Appendix III: Temporal variations in pH at different sites during the study period.

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	7.81	7.65	7.60	7.10	7.38
February	8.26	8.11	7.83	7.46	7.90
March	6.22	6.45	6.50	6.24	6.29
April	6.69	6.41	6.42	6.01	5.90
May	7.38	7.34	7.36	7.44	7.56
June	8.47	8.41	8.39	8.24	8.11
July	7.77	7.80	7.91	7.82	8.15
August	8.27	7.88	8.04	8.02	7.90
September	7.80	7.79	7.64	7.79	7.52
October	8.52	7.08	7.55	7.38	7.80
November	8.85	8.47	8.50	8.60	8.46
December	8.59	8.55	8.36	8.04	7.71

Appendix IV: Temporal variations in turbidity (NTU) at different sites during the study period.

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	6.13	6.20	6.67	16.53	10.93
February	6.90	5.40	8.00	8.70	10.57
March	12.70	5.13	6.30	19.07	19.67
April	27.43	13.30	14.10	80.27	95.90
May	58.77	85.00	92.17	86.27	95.03
June	60.67	95.24	98.38	76.28	88.56
July	67.50	169.67	104.67	64.43	34.80
August	65.13	114.67	89.57	56.50	30.23
September	61.07	96.93	66.47	38.47	58.00
October	42.67	76.27	30.90	27.07	64.27
November	50.50	55.13	41.33	57.40	72.23
December	38.50	47.87	37.40	42.40	52.30

Appendix V: Temporal variations in electrical conductivity (μs cm^{-1}) at different sites during the study period.

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	103.77	107.37	108.80	110.67	106.93
February	113.57	94.53	109.17	113.70	117.07
March	139.23	114.97	117.87	117.27	125.40
April	111.80	117.03	112.30	112.73	92.00
May	111.33	105.67	115.67	135.90	124.30
June	116.50	105.10	111.40	107.67	89.70
July	118.40	98.43	110.50	135.53	138.53
August	163.63	111.87	117.40	100.47	131.57
September	168.83	102.77	96.03	136.17	119.40
October	130.93	141.30	112.83	111.63	155.30
November	122.47	110.80	105.30	105.57	100.77
December	111.27	107.67	108.33	110.40	107.03

Appendix VI: Temporal variations in water depth (m) at different sites during the study period.

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	10	22	11	8	7
February	10	26	15	8	10
March	9	21	18	7	7
April	11	23	32	8	11
May	11	28	25	8	8
June	11	21	24	8	8
July	11	19	28	7	9
August	11	23	29	7	8
September	8	20	22	5	3
October	10	22	18	5	6
November	11	21	13	8	7
December	11	23	17	8	7

Appendix VII: Temporal variations in Mn (mg kg^{-1}) levels in sediments

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
July	437.50	242.92	423.33	138.75	323.75
August	287.50	267.78	346.57	296.25	430.00
September	831.25	297.50	297.50	154.74	319.58
October	820.00	658.75	867.50	271.25	937.50
November	732.50	823.75	803.75	351.25	785.00
December	745.56	798.75	888.75	342.50	823.75

Appendix VIII: Temporal variations in Cu (mg kg^{-1}) levels in Common Carp muscles

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	0.10	2.67	0.00	2.17	0.50
February	3.07	3.67	0.00	1.63	0.27
March	2.87	1.00	0.00	2.00	0.50
April	2.47	0.23	1.03	1.03	1.19
May	0.48	1.00	0.00	0.50	1.30
June	1.53	1.00	0.77	0.80	0.80
July	2.92	0.45	0.58	0.93	0.56
August	0.59	0.64	0.30	0.48	0.53
September	0.75	0.45	0.85	0.55	0.61
October	0.39	0.75	0.93	0.68	0.25
November	1.08	0.81	0.91	0.84	0.95
December	0.31	0.37	0.85	1.03	0.65

Appendix IX: Temporal variations in Cu (mg kg^{-1}) levels in African Catfish muscles

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	0.625	1.050	0.525	0.43	1.53
February	0.775	0.375	0.725	0.70	1.00
March	0.275	0.975	0.575	1.18	1.40
April	0.850	1.675	0.717	1.06	0.53
May	1.150	1.950	1.125	0.33	0.13
June	0.800	0.350	1.725	2.30	2.04
July	0.675	0.575	0.550	0.71	0.23
August	1.275	1.550	1.125	0.77	0.36
September	2.475	1.525	0.250	0.80	0.28
October	0.438	0.538	0.038	1.09	0.48
November	0.788	0.563	0.200	1.75	0.56
December	0.625	0.263	0.588	0.59	0.95

Appendix X: Temporal variations in Cu (mg kg^{-1}) levels in Tilapia muscles

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	1.040	0.70	0.57	0.63	0.63
February	1.030	0.53	0.63	0.60	0.70
March	1.050	0.78	0.90	0.73	0.43
April	1.175	0.35	0.78	0.90	0.93
May	1.080	0.70	1.00	0.30	0.83
June	1.050	1.31	1.40	0.20	1.09
July	0.792	0.83	0.59	1.30	1.25
August	0.575	0.10	1.09	1.02	0.55
September	0.358	0.48	0.53	0.54	1.04
October	0.550	0.19	0.28	0.48	0.11
November	0.338	0.11	0.13	0.51	0.11
December	0.350	0.13	0.63	0.47	0.93

Appendix XI: Temporal variations in Zn (mg kg^{-1}) levels in Common Carp muscles

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	74.633	29.97	51.23	71.35	36.30
February	57.100	35.50	26.87	55.50	37.53
March	62.700	59.43	32.37	55.47	47.47
April	35.323	43.67	62.33	84.73	48.43
May	37.370	42.60	54.90	72.40	72.63
June	55.133	56.03	48.13	62.67	66.30
July	37.000	47.00	42.33	51.67	50.33
August	60.000	36.67	55.33	52.33	45.00
September	48.000	38.67	32.00	55.00	37.00
October	21.913	47.35	20.94	81.48	66.79
November	31.550	50.88	24.40	52.65	37.04
December	51.067	45.33	22.75	51.55	39.90

Appendix XII: Temporal variations in Zn (mg kg^{-1}) levels in Catfish muscles

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	35.60	41.60	23.90	29.05	20.90
February	33.00	31.70	28.50	28.20	17.06
March	25.00	29.35	41.50	31.68	47.90
April	42.80	37.00	35.27	47.83	27.30
May	39.80	35.20	45.80	52.53	46.67
June	31.50	30.90	38.20	49.00	34.63
July	26.00	39.75	32.00	35.33	61.00
August	53.00	55.00	57.00	59.50	32.50
September	38.00	27.00	28.00	31.00	20.67
October	21.34	20.96	44.69	27.63	29.60
November	28.95	25.69	36.73	33.14	30.93
December	33.00	22.69	34.88	34.88	26.00

Appendix XIII: Temporal variations in Zn (mg kg^{-1}) levels in Tilapia muscles

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	37.00	39.250	30.70	37.70	17.50
February	25.60	26.890	42.60	34.60	31.60
March	33.00	37.250	47.10	34.00	37.10
April	24.24	41.900	31.00	39.50	34.45
May	26.60	51.200	33.00	46.10	54.63
June	41.90	57.500	54.33	55.90	33.10
July	30.00	34.000	36.00	48.00	39.00
August	27.00	29.000	32.00	32.00	37.00
September	29.00	40.000	26.50	43.00	37.00
October	25.90	42.000	18.69	25.85	44.50
November	30.00	33.000	26.20	21.95	40.38
December	25.50	24.000	20.00	28.50	22.31

Appendix XIV: Temporal variations in Pb (mg kg^{-1}) levels in Common Carp muscles

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	0.670	1.49	1.08	1.15	0.30
February	1.230	1.28	1.38	0.13	1.14
March	1.111	1.58	1.50	1.58	0.70
April	1.158	0.50	1.64	1.53	0.94
May	3.275	0.98	0.97	1.33	1.18
June	3.050	0.68	1.43	1.36	1.48
July	1.210	1.14	1.27	1.47	0.91
August	1.450	1.51	1.14	1.46	1.30
September	0.990	0.93	0.94	1.45	0.84
October	0.730	0.44	1.16	1.28	1.17
November	1.550	1.82	1.68	1.25	1.33
December	0.670	0.59	0.91	0.37	0.64

Appendix XV: Temporal variations in Pb (mg kg^{-1}) levels in African Catfish muscles

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	0.719	0.800	0.901	0.575	1.10
February	0.767	1.025	1.100	0.610	1.56
March	0.775	1.558	1.000	0.667	0.77
April	0.000	0.719	1.850	0.658	0.28
May	0.608	0.675	1.916	1.191	1.52
June	0.859	1.225	1.103	1.367	1.20
July	0.475	0.900	0.675	1.467	0.84
August	0.800	1.050	0.775	1.254	0.88
September	0.597	0.708	1.650	0.989	1.16
October	0.497	0.497	0.644	0.838	1.15
November	1.000	0.438	0.539	0.870	1.39
December	0.616	0.775	0.536	1.075	1.08

Appendix XVI: Temporal variations in Pb (mg kg^{-1}) levels in Tilapia muscles

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	0.213	1.026	0.97	0.51	0.00
February	0.825	0.561	0.45	0.45	0.68
March	0.211	0.874	0.44	0.39	0.93
April	0.758	0.356	0.98	0.74	0.00
May	0.475	1.017	0.00	0.91	0.00
June	1.567	1.308	0.57	0.32	1.08
July	1.242	0.450	0.29	0.71	0.71
August	1.000	0.740	1.07	1.03	0.26
September	0.578	0.250	0.95	0.73	0.85
October	0.496	0.604	0.75	0.58	0.95
November	1.131	0.463	0.14	0.93	0.79
December	0.679	0.554	0.71	0.50	0.38

Appendix XVII: Temporal variations in Cr (mg kg^{-1}) levels in Common Carp muscles

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	0.525	0.32	0.46	0.63	0.00
February	0.73	0.27	0.25	0.34	0.45
March	0.690	0.13	0.40	0.36	0.27
April	0.083	1.71	0.75	0.50	0.00
May	1.150	1.08	0.6	1.24	0.34
June	0.975	1.00	0.95	0.96	1.00
July	0.780	0.56	0.87	0.69	0.56
August	0.890	0.78	0.49	0.50	0.39
September	0.580	0.84	0.73	0.47	0.00
October	0.808	0.37	0.83	0.63	0.88
November	0.663	0.38	1.16	0.52	0.00
December	0.40	0.48	1.03	0.44	0.00

Appendix XVIII: Temporal variations in Cr (mg kg^{-1}) levels in African Catfish muscles

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	0.900	0.600	0.675	1.200	0.68
February	1.000	0.950	0.875	1.225	0.48
March	0.375	1.075	0.825	0.925	0.20
April	0.625	1.075	0.258	0.283	0.48
May	0.975	1.65	0.800	0.642	0.63
June	0.775	0.975	1.025	0.658	0.49
July	0.679	0.985	0.460	0.535	0.30
August	0.941	0.20	0.675	0.645	0.68
September	1.025	0.732	0.750	0.50	0.48
October	1.55	1.125	0.925	0.838	0.78
November	0.925	0.488	0.737	0.925	1.05
December	0.40	0.438	1.113	1.113	0.56

Appendix XIX: Temporal variations in Cr (mg kg^{-1}) levels in Tilapia muscles

Month/Site	Kathini	Mathauta	Manyatta	Riakanau	Tumutumu
January	0.750	0.775	0.53	0.78	0.95
February	0.675	1.075	0.75	0.70	1.02
March	0.450	0.900	0.73	1.00	1.05
April	0.850	1.225	0.70	1.00	0.68
May	0.625	0.800	0.90	0.35	0.45
June	0.825	0.450	1.03	0.03	0.45
July	0.467	0.600	1.83	0.64	0.38
August	0.475	0.675	0.40	0.16	0.43
September	0.200	0.950	0.60	0.33	0.26
October	0.775	0.713	1.15	0.55	0.69
November	0.338	0.575	0.43	0.53	0.64
December	0.275	0.413	0.46	0.45	0.84