

**AN ASSESSMENT OF HEAVY METAL CONCENTRATIONS IN SURFACE
SEDIMENTS, WATER AND COMMON CARP (*Cyprinus carpio* Linnaeus, 1758) IN
LAKE NAIVASHA, KENYA**

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**A Thesis Submitted to the Graduate School in Partial Fulfillment for the Requirement of
the Award of Degree of Master of Science in Environmental Science of Egerton University**

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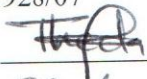
DECLARATION AND RECOMMENDATION

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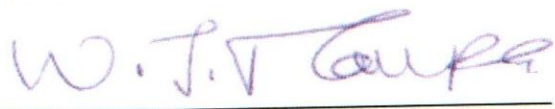
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ABSTRACT

Sediments act as significant archives for eco-toxicological information due to their potential ability of sinking contaminants. Water on the other hand is critical in dissolution and transportation of heavy metals whilst *Cyprinus carpio* (common carp), a fish delicacy (constituting about 89% of Lake Naivasha fishery) in Lake Naivasha feeds on benthivorous material and has the potential of accumulating heavy metals. With the tremendous increasing human activities in the catchment and around the Lake there could be elevated release and transportation of heavy metals from the catchment and subsequent accumulation in the lake water, sediments and *C. carpio*. An investigation of the cadmium, copper and lead concentrations in water, sediments and the common carp (*Cyprinus carpio*) muscle tissues was undertaken in Lake Naivasha. Seven purposive sampling sites were established within the Lake based on proximity to human activities, and three replicate samples of water, sediments and *C. carpio* muscle tissues collected from each site. The concentration of the metals was thereafter measured by use of an AAS. Descriptive and inferential statistics was used to summarize the concentration of heavy metals in sediments, water and *C. carpio* muscle tissues as arithmetic mean with standard deviation and to compare the concentrations of copper, lead and cadmium in sediments, water and *C. carpio* muscle tissues with the recommended international standards. Mean cadmium concentration ranged from 1.2 – 5.4 mg/kg in sediments, 10.0 – 10.1 µg/l in water and 1.1– 1.7 mg/kg in *C. carpio* muscle tissues, Mean copper concentration ranged from 3.0 – 8.4 mg/kg in sediments, 30.0 – 32.3 µg/l in water and 1.5– 2.2 mg/kg in *C. carpio* muscle tissues. Lead was the most predominant heavy metal recorded with the ranges 17.1– 53.1 mg/kg in sediments, 100.0 – 179.8 µg/l in water and 5.2– 58.1 mg/kg in *C. carpio* muscle tissues. In sediments, mean cadmium concentration exceeded the NOAA TEC Sediment Quality Guidelines. In *C. carpio* muscle tissues, mean cadmium and lead concentration was predominantly higher than the tolerable values in fish; whilst in water, only lead concentration was beyond the WHO HDL in drinking water. Recorded heavy metal concentrations were significantly different (One way ANOVA) in most sampling stations at 5% significance level ($P < 0.05$) with elevated heavy metal levels in sediments followed by *C. carpio* muscle tissues and water. The implication could be of chronic effect to higher trophic biota. Continuous assessment, monitoring and management of Cd, Cu and Pb concentration in Lake Naivasha is therefore recommended to enhance conservation of ecological resources within the Ramsar site.

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ACRONYMS

Cd	Cadmium
Cu	Copper
D.O.S	Directorate of Overseas Surveys
EC	European Commission
HDL	Highest Desirable Level
HM	Heavy Metals
IAEA	International Atomic Energy Agency
KEMFRI	Kenya Marine and Fisheries Research Institute
LEL	Lowest Effect Level
MPL	Maximum Permissible Level
NL	Not in literature cited
NOAA	National Oceanic and Atmospheric Administration
Pb	Lead
SEL	Severe Effect Level
TC	Threshold Concentration
TEC	Threshold Effect Concentration
UNEP	United Nations Environmental Programme
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
WWF	World Wide Fund for Nature

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Heavy metals are metals having a density of 5 g/cm³ or greater. These metals include elements such as copper, cadmium, lead, selenium, arsenic, mercury, and chromium (McGeer *et al.*, 2000). High levels of lead (density 11.34 g/cm³), copper (density 8.92 g/cm³) and cadmium (density 8.65 g/cm³) can act as ecological toxins in aquatic systems (Allen, 1995). Excess heavy metal levels in surface water pose health and ecological risks to humans and the environment. The World Health Organization (WHO) and the Food and Agriculture Organization (FAO) state that monitoring the concentrations of lead, copper and cadmium particularly in ecological systems is obligatory since they are trace elements and are toxic even at low levels due to their accumulative concentration (Staniškienė *et al.*, 2009). Unlike other classes of pollutants, which can be biodegraded and destroyed completely, heavy metals are non-biodegradable (Allen, 1995). They permeate the environment by various means, penetrate the circle of metabolism, become toxic and disturb physiological functions of organism. Heavy metals are released into the environment as a result of natural and anthropogenic processes (Forstner and Wittmann, 1983). Anthropogenic derived metals enter the fluvial systems from both point and diffuse sources. Point sources include industrial discharges and sewage treatment works whereas diffuse sources include farming and atmospherically transported material delivered to the catchment by dry and wet deposition (Staniškienė *et al.*, 2009). Studies on heavy metals in lakes, fish and sediments have been a major environmental focus especially in the last decade (Ochieng *et al.*, 2007; Ozturk *et al.*, 2009; Weis and Weis, 1995). Sediments are important sinks for various pollutants like heavy metals and also play a significant role in the mobilization of contaminants in aquatic systems under favorable conditions and in interactions between water and sediment (Klavins *et al.*, 2000).

Lake Naivasha is a freshwater lake, with no surface outlet, located in the Eastern Rift Valley of Kenya. Being situated at the basin of the Rift Valley, it functions as a sink for pollutants thereby experiencing notable anthropogenic stresses (Kamau *et al.*, 2008). Tarras-Wahlberg *et al.*, (2002) reported massive brown clay and sandy mud units in the surface sediments near the mouth of the Malewa River as it enters the lake. The observed clay is interpreted as a deltaic deposit (that is mud flat), which is being actively eroded by wave action.

Sediments in lakes can conserve important environmental information (Von Gunten *et al.*, 1997), being both a carrier of, and a possible source of, contaminants to aquatic systems (Kamau *et al.*, 2008). *C. carpio* faces some eco-toxicological threats much of which is as a result of toxic chemical pollutants from agriculture, industry and sewage out falls into Lake Naivasha (Kamau *et al.*, 2008). *C. carpio* is a benthivore and thus likely to be exposed to heavy metals. This feeding behaviour poses a risk of bio-accumulation and bio-magnification in their tissues and up the trophic chain. This can cause adverse effects over time resulting in loss of biodiversity. A recent study on heavy metal concentrations in Lake Naivasha indicated lead, cadmium and copper concentrations at 25.34 $\mu\text{g/g}$, 0.73 $\mu\text{g/g}$ and 10.33 $\mu\text{g/g}$ dry weights in sediments (Ochieng *et al.*, 2007). Dissolved trace metal concentrations in water were recorded at 8 $\mu\text{g/l}$ of cadmium, 4.7 $\mu\text{g/l}$ of copper and 42.1 $\mu\text{g/l}$ of lead (Ochieng *et al.*, 2007). These findings clearly indicated the need to continue monitoring the heavy metal concentrations overtime to establish their potential impact on aquatic resources and inform decision-makers on important management and conservation measures to be undertaken. Such measures would be directed at the catchment, where there is intensive use of agrochemicals containing heavy metals, in order to reduce heavy metal use and haphazard discharge into the lake.

Studies of the input of nutrients and other contaminants from the Naivasha catchment to the lake have been undertaken by many researchers (for example. Gaudet and Muthuri, 1981; Hubble and Harper, 2002; Kitaka *et al.*, 2002a). However, only few studies (for example Wandiga *et al.*, 1983; Kamau *et al.*, 2008; Ochieng *et al.*, 2007) have investigated heavy metals in the lake but with less focus on the spatial and temporal fluctuations of heavy metals and their likely impacts on *C. carpio* that constitutes more than 90% of the lake's fisheries. The principal aim of this study was therefore to provide data that is essential for Lake Naivasha resources management and conservation by investigating the variation of heavy metal concentrations in lake water, sediments and in *C. carpio* muscle tissues. This is expected to serve as a basis in the planning and management of fisheries in Lake Naivasha.

1.2 Statement of the problem

In the last two decades, Lake Naivasha basin has increasingly been degraded by human beings through haphazard disposal of effluents containing toxic substances. The lake basin and its surroundings support an intensively irrigated agricultural land ranging from horticultural and

floricultural farms, small scale farms, a fast-growing township and industries. Wastes generated from these human activities are carried to the lake by run offs leading to water quality deterioration. The effluents into the lake vary in composition and quantity. Some of these substances are heavy metals that have lately become an issue of environmental and human health concern. This is because of their toxicity even at low levels which can accumulate in the higher trophic levels and affect the physiological functioning of an organism(s). Due to the fact that the lake is shallow and has no surface outlet, much of the wastes drain and collect into the lake thereby increasing heavy metal concentration in sediment, water and fish. Fish, particularly benthivorous species like *C. carpio* and organisms up its trophic chain are more likely to be impacted adversely by the heavy metals as it forms a major component of the Lake Naivasha fishery consumed by majority of the population in Naivasha. Although much research has been done in Lake Naivasha, none has directly related heavy metal concentrations in sediments, water and fish, hence the importance of this study. This study therefore sought to assess the concentrations of cadmium, lead and copper in water and sediments and compare them to those in *C. carpio* muscle tissues in Lake Naivasha to establish the variation.

1.3 Objectives

1.3.1 Broad objective

The broad objective of this research was to assess the concentration of cadmium, lead and copper in sediment, water and *C. carpio* muscle tissues from Lake Naivasha, Kenya and determine any variation in their concentrations.

1.3.2 Specific objectives

1. To determine the concentrations of cadmium, lead and copper in sediment samples from Lake Naivasha.
2. To determine the concentrations of cadmium, lead and copper in water samples from Lake Naivasha.
3. To determine the concentrations of cadmium, lead and copper in *C. carpio* muscle tissues from Lake Naivasha.
4. To compare the concentrations of cadmium, lead and copper in water, sediments and *C. carpio* muscle tissue from Lake Naivasha with the recommended international standards.

5. To establish the variation between heavy metal concentrations in lake sediments, water and in *C. carpio* muscle tissues from Lake Naivasha.

1.4 Research Questions

1. What are the concentrations of cadmium, lead and copper in sediment samples from Lake Naivasha?
2. What are the concentrations of cadmium, lead and copper in water samples from Lake Naivasha?
3. What are the concentrations of cadmium, lead and copper in *C. carpio* muscle tissues from Lake Naivasha?
4. How do the concentrations of cadmium, lead and copper in sediments, water and *C. carpio* muscle tissues compare with the recommended international standards?
5. What is the variation between heavy metal concentrations in lake sediments, water and in *C. carpio* muscle tissues?

1.5 Justification of the study

Kenya's Lake Naivasha, is a wetland of international importance recognized by the Ramsar Convention and a historically renowned hot spot for tropical biodiversity. Fish harvests in the lake particularly of the popular tilapia have in the past few years declined greatly and fishermen are now relying on the newly introduced common carp (*C. carpio*). *C. carpio* contributes about 95 – 97% (Mr. Kamau: Fisheries Officer, Naivasha, Personal Communication, October 2009) of the total fish catch in Lake Naivasha with the rest comprising of *Tilapia zillii*, *Oreochromis leucostictus*, *Micropterus salmoides* and *Barbus palidamus*. However, pollutant discharge into the lake has increased the potential for heavy metal accumulation in *C. carpio* due to its characteristic feeding behavior that involves sucking in sediments with prey items and retaining food organisms whilst sediment particles are expelled (Hickley *et al.*, 2004). Sediments act as sinks for pollutants and *C. carpio* feeding on them poses a great risk of pollutant transmission into its system. Considering the economic importance of *C. carpio* in Lake Naivasha, a study on heavy metal concentration in sediments, water and *C. carpio* is of great importance. Additionally, heavy metals have been shown to have negative effects on aquatic organisms (Ogendi *et al.*, 2007a and b; Staniškienė *et al.*, 2009) as well as humans hence both

the World Health Organization and the Food and Agriculture Organization suggest their obligatory monitoring (Staniškienė *et al.*, 2009). Copper, lead and cadmium are very toxic and have been subjects of eco-toxicological research for a long period of time, hence the need to study their concentrations overtime as they tend to bio-accumulate in living things faster than they are metabolized. Due to its domination in Lake Naivasha, *C. carpio* is the main fish consumed by people living around Naivasha. In addition, fish eating birds of prey like the African fish eagle (*Haliaeetus vocifer*) find delicacy in the fish. Upon consumption of contaminated *C. carpio*, there is the likelihood that human health may also be impaired with serious future consequences. Considering that in Kenya, health issues pose a serious challenge and especially the modern environmental health hazards which are difficult to detect, and expensive to treat. In humans for example, long-term exposure to cadmium is associated with renal dis-functions. High exposure can lead to obstructive lung disease and has been linked to lung cancer. Cadmium may also produce bone defects (osteomalacia, osteoporosis) in humans and animals. In addition, the metal can be linked to increased blood pressure and effects on the myocardium in animals (Nawrot *et al.*, 2006). High levels of lead exposure may also result in toxic 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 (Davydova, 2005; Grandjean and Landrigan, 2006). Long-term exposure to copper on the other hand can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhoea. Catalytic copper, because of its mobilization and redox activity, is believed to play a central role in the formation of reactive oxygen species that bind very fast to DNA, and produce damage by breaking the DNA strands or modifying the bases and/or deoxyribose leading to carcinogenesis (Theophanidesa and Anastassopouloub, 2002). Other ecological components in its food chain may also face eco-toxicological threats. In *C. carpio*, the study focused on heavy metal analysis on the muscle tissues as they are the fatty and edible parts in the fish where heavy metals tend to accumulate. Despite being the most polluted lake in the area (Ochieng *et al.*, 2007; Gitahi *et al.*, 2002), Lake Naivasha remains an important source of water for flower farms and the people living in the surrounding and their livestock. A number of fishermen and their families depend on the lake resources. There is a lot of pressure on the declining resource as a population of 650,000 persons was recorded in the Lake Basin in 2009 of which 160,000 people live around

the Lake itself (WWF, 2010). This has called for more water abstraction which is estimated at $3 \times 5 \times 10^6 \text{ m}^3$ per month, with about 250 boreholes (Alfarra, 2004). This greatly threatens the sustainable use of the lake. The lake is also a source of income and revenue to the Naivasha municipal council. The findings of this study will be of great use to the stakeholders of Lake Naivasha since the results will be used to assist in planning the management programmes for sustainable use of Lake Naivasha, in addition to informing policies meant to protect human and environmental health against the adverse effects of heavy metals.

1.6 Operationalization of terms

Bio-magnification: This refers to the bioaccumulation and amplification of a substance up the food chain by transfer of residues of the substance in smaller organisms that are food for larger organisms in the food chain. It generally refers to the sequence of processes that result in higher concentrations of a substance in organisms at higher trophic levels. Heavy metals are non-biodegradable hence tend to bioaccumulate and biomagnify up the trophic levels

Bio-accumulation: This refers to the accumulation of substances, such as pesticides, heavy metals or other organic chemicals in an organism. Bio-accumulation occurs when an organism absorbs a toxic substance at a rate greater than that at which the substance is lost thus, the longer the biological half-life of the substance, the greater the risk of chronic poisoning, even if environmental levels of the toxin are not very high.

Eco-toxicology: A scientific discipline combining the methods of ecology and toxicology in studying the effects of toxic substances and especially pollutants on the environment

Heavy metal: A heavy metal is a member of an ill-defined subset of elements with a density of 5 g/cc or greater that exhibits metallic properties, such as copper, lead and cadmium. They are hazardous pollutants due to the speed of their dissemination in the biosphere and their accumulative concentration. Even at low levels, they permeate the environment by various means, penetrate the circle of metabolism, become toxic and disturb physiological functions of an organism.

Common carp (*Cyprinus carpio*): The Common carp (*Cyprinus carpio*) is a widespread large bottom feeding (benthivorous) freshwater fish having a body covered with cycloid scales, a naked head, one long dorsal fin, and two barbels on each side of the mouth. It is native to Asia

and inhabits ponds and sluggish streams and is often raised for food. It has been introduced into environments worldwide, and is often considered an invasive species.

Sediments: Sediment is any particulate matter that can be transported by fluid flow, and which eventually is deposited. They act as sinks for heavy metals and many other pollutants.

Copper: Copper is a chemical element with the symbol Cu (Latin: *cuprum*) and atomic number 29. It is a ductile metal with very high thermal and electrical conductivity.

Lead: Lead is a soft ductile dense metallic element with symbol Pb (Latin: *plumbum*) and atomic number 82.

Cadmium: Cadmium is a chemical element with the symbol Cd and atomic number 48. The soft, bluish-white transition metal is chemically similar to the two other metals in group 12, zinc and mercury.

1.7 Scope of the study

The study sought to assess the concentrations of copper, lead and cadmium in water, sediments and *C. carpio* muscle tissues from seven sampling stations in Lake Naivasha and further establish any significant variation among the heavy metal concentrations in water and sediments and those measured in *C. carpio* muscle tissues from the different sampling stations. Five sample stations were selected to represent areas of anthropogenic influence while two were to represent undisturbed sites. Sampling was randomly conducted four times between the periods March and May 2010 to obtain representative data. Water and sediment sampling was restricted to surface waters and sediments as the study was an ecological survey. In *C. carpio* analysis was based on the muscle tissues as they are the fatty complexes that tend to accumulate heavy metals. The Lake Water pH, temperature, light transparency, water conductivity, total dissolved solids, and dissolved oxygen were also measured from each sampling site during every sampling period as these are important limnological parameters that alter the concentration of heavy metals and in most cases increase their toxicity levels.

CHAPTER TWO

LITERATURE REVIEW

Heavy metals are high priority pollutants because of their relative high toxicity and persistent nature in the environment. Knowledge of their changing concentrations and distribution in various compartments of the environment is pertinent for effective environmental programmes worldwide. The contamination of fresh waters with a wide range of pollutants has become a matter of concern over the last few decades (Vutukuru, 2005). The natural fresh water aquatic systems may extensively be contaminated with heavy metals released from domestic, industrial and other man-made activities (Velez and Montoro, 1998). Trace elements are some of the main sources of metal toxicity problems in the aquatic environment since most of the aquatic organisms are not adapted to deal with them when they occur above threshold concentrations. The most toxic ones such as Pb, Cu and Cd have been subjects of eco-toxicological research for a long period of time (Chan 1995a, b; George and Pirie 1984; Gold-Bouchon *et al.*, 1995; Hodson, 1981; Howarth and Sprague 1978; Wong *et al.*, 1995). Some of the toxic effects of heavy metals in aquatic organisms which have been reported include bioaccumulation in various organs, tissue damage (for example in oysters), disruption in growth and reproduction (e.g. in marine bivalve *Cerastoderma edule*) and induction and synthesis of metallothionein (Bowner *et al.*, 1994; Chan 1995b; Gold- Bouchon *et al.*, 1995; Lim *et al.*, 1995).

In lakes, the characteristics of the water, such as acidity or the amount of organic matter, are known to be important factors in determining the fate of heavy metals (Bols *et al.*, 2001). Increased loading of heavy metals into lakes may have several ecological consequences (Canli, 1995). Elevated trace metal concentrations may lead for example, to toxic effects or bio-magnification in aquatic environments (Canli and Kalay, 1998). Accumulation of heavy metals in the food web/chain can occur either by bio-concentration from the surrounding medium such as water or sediment or by bioaccumulation from the food source (Clarkson, 1998). Aquatic organisms have been widely used in biological monitoring and assessment of safe environmental levels of heavy metals (Filipovic and Raspor, 2003; Farombi *et al.*, 2007; Ogendi *et al.*, 2007b). Heavy metals may injure fish receptors and impair perception – especially olfaction and vision. This may disturb prey search and capture, and result in malnutrition as well as swimming and balancing disorders (Farombi *et al.*, 2007).

2.1 Sources and accumulation of heavy metals in water and sediment in lakes

Studies on heavy metals in lake sediments have been a major environmental focus especially in the last decade. Heavy metals are natural constituents of natural waters and some of the essential ones such as Fe, Mn, Zn, Co, Mo, Se and Cu are present at low concentrations and are biologically important in the aquatic environment. They enter natural waters from various sources. The natural geological weathering of rocks and soil, directly exposed to surface waters, is usually the largest natural source. The other main source of heavy metals is anthropogenic input from domestic, farming, mining, and other industrial manufacturing activities such as corrosion of copper tubing and discharge of waste water from electroplating smelting and metal engraving industries. Once they are in the aquatic environment, metals are adsorbed onto inorganic and organic particulate deposits and are incorporated into sediment resulting in elevated levels of heavy metals in bottom sediment (Chan 1995a, b; Cheevaporn *et al.*, 1995; Jeon *et al.*, 2003; Schmitt *et al.*, 2003).

The role of inland waters as receptors of a variety of industrial and municipal waters containing varying loads of trace metals implies that concentrations of trace metals, their chemical forms and fluxes within these impacted ecosystems should be known. In addition, knowledge of the physico-chemical parameters of natural waters such as pH, temperature and turbidity is pertinent because these parameters can modify toxicities of various heavy metals and therefore indicate the water quality of the ecosystems. Although developing countries have, in the past, been considered least polluted, rapid industrial development and high population growth rates in the past decades have gradually degraded water quality of some of the natural waters of these countries (Berg *et al.*, 1995; Chan 1995a, b; Cheevaporn *et al.*, 1995; Lim *et al.*, 1995). Knowledge of concentration of heavy metals is desirable for the estimation of metal concentration in lake's water, sediment and biota (Lowe and Niinu, 1984). Heavy metals accumulated in benthic organisms may be further bio-accumulative in food webs (McGeer *et al.*, 2000). As rivers drain in a lake, the decrease of velocity results in sediment deposition (Menezes and Qasim, 1984). Such investigations may be used to determine both the character of contamination and, if sedimentation rates are known, changes in contaminant loading with time (Reinberg and Schreck, 1986; Nicholson, 1996). The WHO drinking water standards (1993), recommend the highest desirable levels of copper, lead and cadmium in natural waters as 50 µg/l, 50 µg/l and 10 µg/l in natural waters. In sediments, the threshold concentrations of copper,

lead and cadmium are 31.6 mg/kg, 35.8 mg/kg and 0.99 mg/kg respectively, according to National Oceanic and Atmospheric Administration (NOAA, 2009) sediment quality guidelines.

It is generally acknowledged that heavy metals in their dissolved ionic state control direct toxic effects (Förstner, 1983; 1988; Stumm and Morgan, 1996). However, in aquatic systems, they are usually predominantly associated with sediments (Förstner, 1983; Windom *et al.*, 1991). Therefore, the concentration of heavy metals in sediment is generally a more sensitive and accurate indicator of contamination of an aquatic system, compared to the concentration of dissolved metals (Carelli *et al.*, 1995). It is also recognized that sediment-bound heavy metals have the potential of changing to the ionic state (Willford *et al.*, 1987).

2.2 Accumulation of Heavy Metals in Fish

Heavy metal contamination may have devastating effects on the ecological balance of the recipient environment and a diversity of aquatic organisms (Farombi, *et al.*, 2007). Among animal species, fish are the inhabitants that cannot escape from the detrimental effects of these pollutants (Olaifa *et al.*, 2004). Fish are widely used to evaluate the health of aquatic ecosystems because pollutants build up in the food chain and are responsible for adverse effects and death in the aquatic systems (Farkas *et al.*, 2002). Campbell *et al.*, (2003) reported that the tilapiine species in the Kenyan Rift valley lakes, including the Nile tilapia *Oreochromis niloticus*, had consistently low total mercury (THg) concentrations ranging between 2 and 25 ng g⁻¹. THg concentrations in the fish muscle tissues were generally below those of World Health Organization's recommended marketing limit of 200 ng g⁻¹ for at risk groups and 500 ng g⁻¹ recommended European Economic Limit. Elevated levels of lead and Cadmium were also recorded in *C. carpio* muscle tissue heavy metal studies in Madivala Lake, Karnataka (Abida *et al.*, 2009). The studies carried out on various fish have shown that heavy metals may alter the physiological activities and biochemical parameters both in tissues and in blood of fish (Farkas *et al.*, 2002). The IAEA – 407 sets recommended tolerable values of 3.28 mg/kg copper, 0.12 mg/kg lead and 0.18 mg/kg cadmium in fish (Wyse *et al.*, 2003).

2.3 Effects of Cadmium, Copper and Lead Accumulation in Fish

In biological systems, cadmium and lead have no known physiological role whereas copper is an essential component of enzymes or metalloproteins in fish metabolism. Heavy

metals accumulate in the tissues of aquatic animals and may become toxic when accumulation reaches a substantially high level. Toxic effects occur when excretory, metabolic, storage and detoxification mechanisms are no longer able to counter uptake. Studies carried out with different fish species have revealed that both essential and non-essential metals can produce toxic effects in fish by disturbing physiological activities, biochemical processes, reproduction and growth and thereafter mortality (Kalay *et al.*, 2000).

2.3.1 Effects of Copper Accumulation in Fish

Copper is essential for the normal growth and metabolism of nearly all organisms, including fish (Payle *et al.*, 1992). However, when biological requirements are exceeded, this metal can become harmful to aquatic biota. Copper is essential as micronutrient for fish and aquatic life, widely used as a very effective algacide and molluscicide (Tao *et al.*, 2001). Since copper from anthropogenic sources eventually contaminates water bodies, toxicity of this metal to aquatic organisms has been intensely studied over the past two decades (Stouthart *et al.*, 1996; Jędrowska and Slominska, 1997). The diet is the major source of copper for fish under optimal growth conditions. High concentrations of copper in combination with low pH are believed to be fatal to fish (Rouleau *et al.*, 1996). Heavy metal accumulation levels in fish tissues increase in connection with exposure period and concentration. However this effect changes according to the type of metal salts and species of organisms. Similarly, copper uptakes from water causes the accumulation of copper in the tissues and organs of fish resulting in effects of the lateral line, olfactory receptors and eyes (Saucier *et al.*, 1991) of newly hatched *C. carpio* larvae (Saucier *et al.*, 1991). The concentrations of copper in fish tissues reflect the amount of bio-available copper in the environment (Waqar, 2006). In fish, the toxicity of copper appears to be inversely related to the tendency of the metal to bind with the fish tissues via ionic interactions. A lower affinity of the fish tissue to copper therefore leads to a greater likelihood of disruption of intracellular processes, which may lead to tissue dysfunction (VonGunten *et al.*, 1997).

The physical and chemical characteristics of water play an important role in copper toxicity for aquatic animals. Copper speciation is directly affected by water pH (Rate and McLaren, 1993). Free cupric ion concentration is higher in water with low pH, whereas copper hydroxide complexes prevail in water with high pH. While copper may form complexes with suspended organic matter, it will ultimately settle out of the water column and be deposited in

the sediment. The toxicity of copper to aquatic organisms is dependent on the speciation of the chemical itself, water hardness and the type and life stage of the exposed organisms (Mis and Higgs, 1997). Among newly hatched fish larvae, even under optimum conditions, various body deformations may occur due to copper toxicity. Usually, only a small percent of larvae show such deformations. However, any adverse environmental factors may induce an increase in their frequency. Various data indicate that environmental conditions such as: temperature below or over the optimum range, pH changes, or nitrate may increase frequency of body deformations in newly hatched Common carp larvae (Kamunde *et al.*, 2002).

2.3.2 Effects of Cadmium Accumulation in Fish

Cadmium is one of the metals most commonly occurring in polluted natural waters which may affect the early stages of fish development (Beattle and Pascie, 1978; Verbost *et al.*, 1989; Basa *et al.*, 2003). The data by various authors shows the adverse effect of cadmium especially on hatchability and quality of larvae (Sangalang and Freeman, 1974; Handy, 1992; Lin and Dunson, 1993; Toth *et al.*, 1995). This metal belongs to the group of highly toxic heavy metals. Naturally, cadmium occurs in water only in trace amounts, but recently its levels have increased due to anthropogenic activities (Szulkowska *et al.*, 1992; Javed, 2003). Most cadmium contamination comes from metal foundries, the dye industry, production of plastics and of accumulators (Beyersmann and Hechtenberg, 1997; Javed, 2005). This exposure results in pathological changes in water ecosystems, mostly demonstrated in fish, which are affected by heavy metals through the respiratory and digestive systems and through the skin (Nogami *et al.*, 2000; Hallare *et al.*, 2005). In general, toxic effects of all heavy metals are similar, including pathological changes in parenchymatous organs and the nervous system. Indeed, long-term exposure of cadmium has some specific effects like impairment of reproductive function and endocrine disruption (Kleiss and Schuetz, 1987; Suresh *et al.*, 1993; Xie and Klerks, 2004). Even at sub-lethal concentrations, cadmium may cause adverse effects in fish, such as abnormal behavior: locomotor anomalies and anorexia (Reader *et al.*, 1989; Javed and Hayat, 1999). Cadmium is also known to damage fish gills, affects blood cells and causes changes in the plasma protein level (Rombough and Garside, 1980; Nogami *et al.*, 2000).

2.3.3 Effects of Lead Accumulation in Fish

Lead exists in several oxidation states, which are of environmental importance (Weber *et al.*, 1991). The divalent form of Pb (II) is the stable ionic form present in the environment and is thought to be the form in which most lead is bio-accumulated by aquatic organisms (Purchase and Fergusson, 1996). Lead enters the aquatic environment through erosion and leaching from soil, lead-dust fall out, combustion of gasoline, municipal and industrial waste discharges, run-off water deposits from streets and other surfaces as well as precipitation (Tessier and Campbell, 1987). It is known to accumulate in the tissues of fish including the bone, muscle tissues, gills, kidneys, liver and scales (Svobodora *et al.*, 2002). According to Cicik and Karayakar, (2004), lead inhibits the impulse conductivity of fish by inhibiting the activities of monoamine oxidase and acetylcholine esterase to cause pathological changes in tissues and organs and impairs the embryonic and larval development of fish species.

Aquatic organisms are sensitive to lead and are affected more strongly by dissolved rather than total lead. Likewise, the toxicity of lead is increased when it forms organo-lead compounds and when environmental conditions consist of high temperature and low pH. Animals are also more sensitive at younger life stages and when exposure durations are greater. The effects of lead increase under rapid growth conditions as illustrated by the increase of the rate of intoxication by lead increased with growth rate, but not fish size (Aardt and Venter, 2004; Andreji *et al.*, 2006).

2.4 Conceptual Framework

Physical, chemical, evolutionary, and ecological processes interacted to produce lakes and their landscapes, including the local and regional biota. However, human beings through their activities have stressed these ecosystems by altering physical habitat, changing the system's food base, changing stream organisms' interactions, and contaminating the water with chemicals. Disposal of contaminants into lakes may increase heavy metal concentration in the sediment, water and fish. Different aquatic organisms often respond to external contamination in different ways, where the quantity and form of the element in water, sediment, or food will determine the degree of contamination. Many dangerous chemical elements, if released into the environment, accumulate in the soil and sediments of water bodies. The lower aquatic organisms absorb and transfer them through the food chain to higher trophic levels, including fish. Hence,

concentrations of heavy metals (HM) in the tissues of fish are determined primarily by the level of pollution of the water and food. Under certain conditions, elements accumulated in the bottom sediments of water bodies can migrate back into the water, hence becoming a secondary source of heavy metal pollution. Changes in the natural levels of some limnological parameters such as pH, conductivity, dissolved oxygen, total dissolved solids, and temperature are also key in altering the concentrations of heavy metals as in most cases they increase toxicity of the heavy metals. (Figure 1).

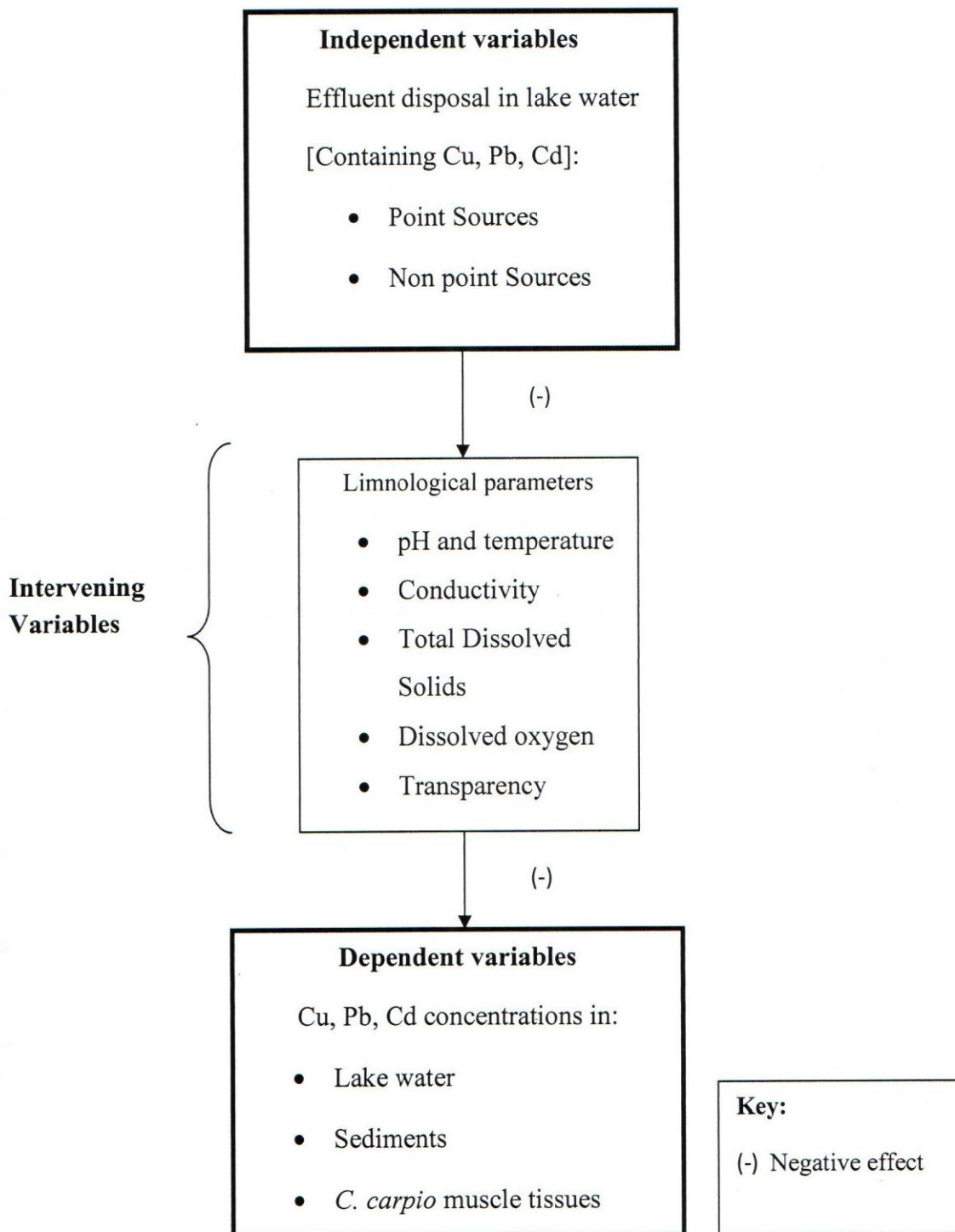


Figure 1: Conceptual framework

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

3.1.1 Catchment and location

The Lake Naivasha has a catchment (see Figure 5) of approximately 3,400km² in area that stretches from the Aberdares mountain ranges in the north and north east to the Olkaria, Longonot Mountains in the south and south east. It is bounded by the Mau escarpment in the west, Eburru to the North and the Kinangop plateau in the East (WWF, 2010). Mean annual temperatures in the basin vary with altitude, ranging from 25°C on the shores of the Lake (1890m asl) to 16°C in the Aberdares Mountains, with average daily temperatures ranging from 5°C to 25°C. The Lake Basin exhibits bimodal rainfall with two rainy seasons in April – May (long rains) and October- November (short rains) at an average range of 1350mm in the Aberdares mountains to 600mm on the shores of the lake. Most of the upper parts of the catchment are considered semi-humid and are suitable for rain fed agriculture, whereas the areas surrounding the Lake are semi-arid (WWF, 2010).

Lake Naivasha (Figure 2) is a shallow, freshwater lake in Kenya's Rift Valley located 190 km south of the equator at an elevation of 1,890 m asl between latitude 0°45' and longitude 36°20'E. It is approximately 100km² in area with a depth of between 3 to 6m, the deepest area being Crescent Island at a maximum depth of 30 m (Britton *et al.*, 2010). The lake is the second-largest freshwater lake in Kenya (after the Kenya portion of Victoria) and forms one of a series of 23 major lakes in the Eastern Rift Valley (Everard *et al.*, 2002b). Rainfall is bimodal with peaks during April and October but shows inter-annual irregularity and an annual evapotranspiration rate which exceeds local rainfall (Kitaka *et al.*, 2002b)

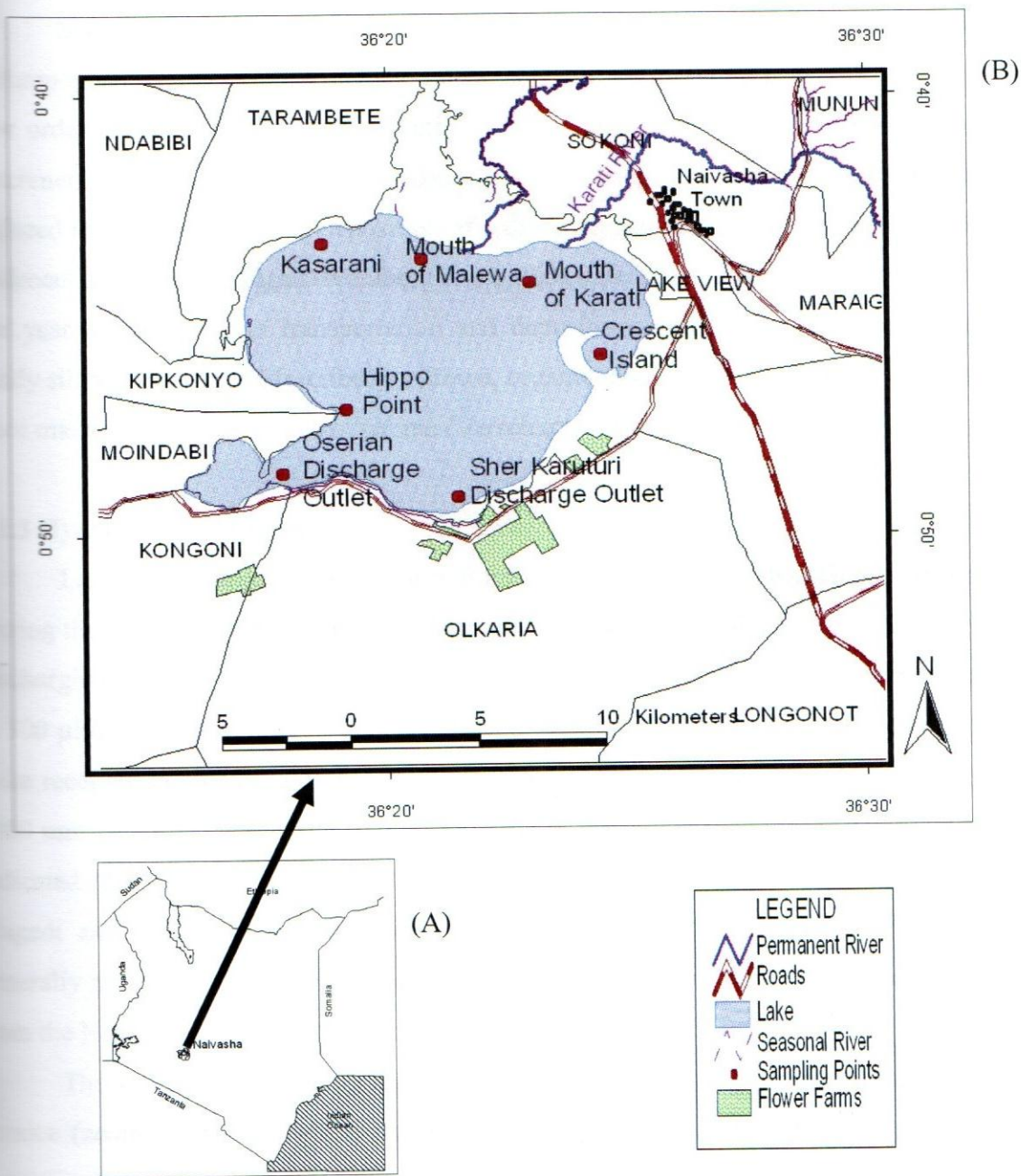


Figure 2: The Lake Naivasha and the study sites. (A) Location of the Lake Naivasha in Kenya, (B) the Lake Naivasha: study sites (1) Hippo point, (2) Kasarani (3) Mouth of Malewa river (4) Mouth of Karati river (5) Crescent Island (6) Sher Karuturi and (7) Oserian. Figures A and B were redrawn from the Survey of Kenya maps, sheet: No.133/4 and 133/2, nominal scale 1:50,000 Series Y731 D.O.S 423, 1975.

3.1.2 Lake Sedimentology

Sediments play key role in influencing Lakes especially as influenced by natural and anthropogenic characteristics of their catchments and surrounding activities. River sediment in low order channels derive from a plethora of hill slope and channel sources in the upstream catchment. Lake Sedimentology in Lake Naivasha is highly variable due to the effects of wind-induced re-suspension and re-deposition of sediments, and the presence of river point sources of sediment in the north (Tarras-Wahlberg *et al.*, 2002). Sedimentation thus occurs between 1-3 cm per year as attributed to transportation and deposition with surface sediments dominated by sandy silt and clay units (described as brown, organic mud). The clay units are a characteristic of trace macrophytes, papyrus and diatoms (Verschuren, 2006).

3.1.3 Hydrology and geology

Lake Naivasha receives its waters from three rivers; the Malewa, Gilgil and Karati rivers. During the sampling period (March to May 2010) only River Malewa and Karati were observed discharging into the Lake. The Lake with no surface outlet remains fresh (Electrical conductivity at 300 $\mu\text{S}/\text{cm}$) as attributed to underground outflow exhibiting a pH of approximately 8.7. The Lake receives an annual rainfall of 600 mm per year with potential evapotranspiration of about 1900 mm per year (Bergner *et al.*, 2003). Ground water levels and isotopic compositions have indicated that the flow is both towards the North and South with significant flows to Lake Magadi and Lake Elementaita, however this takes thousands of years. The water flow is generally away from the Lake with an exception of the western direction where an inflow enters from the Ndabibi plains (Becht *et al.*, 2005).

The geology surrounding the Lake Naivasha is characterized as volcanic ashes rich in pumice (zeolite minerals) which renders them highly permeable with very low water holding capacity. As a result excess irrigation water seeps down to the groundwater. Becht *et al.*, (2005) reported that the soils due to their high permeability and gentle slopes, surface runoff is rare and that most agrochemicals are transported via groundwater. Groundwater thus plays a very important role in the hydrology of Lake Naivasha.

3.1.4 Aspects of biodiversity

Lake Naivasha is located in the Eastern part of the Rift Valley and covers an area of approximately 100km². In 1995, Lake Naivasha was declared a wetland of international importance under the Ramsar Convention (LNRA, 1999). The overall climate of the Eastern Rift Valley is semi-arid. Currently, the lake supports an ecosystem with high but uneven biodiversity, rich in birds (over 400 species, about 100 of which are waterfowl) and plants but no native fish. The lake contains six introduced species of fish and an introduced crustacean species, including *Micropterus salmoides* Lacépède (largemouth bass), *Oreochromis Leucostictus* (Trewewas) (tilapia), *Tilapia zillii* (Gervais), *Cyprinus carpio* (common carp), *Barbus amphigramma* Blgr., *Leticulus reticulate* Peters (guppy) and *Procambrus clarkii* (crayfish). The only endemic fish species *Aplocheilichthys antinorii* (Vinc.) was last recorded in 1962 (Kundu *et al.*, 2010). The artisanal commercial fishery is dependent upon exotic species and is currently in severe decline due to possible accumulated contamination from heavy metal concentration and overfishing. The lake gets its water via three rivers: the Malewa (90% of surface inflows), the Gilgil and Karati. A distinct dry land/savannah flora is represented close to river channels in the lower, temporary rivers, while other plant species are ubiquitous. Fauna biodiversity and abundance appears to be strongly linked to habitat biodiversity as changes in land use patterns and intensity around the Lake can affect its capacity to support rich biological communities (Everard, 2002a). However the Lake has remained fresh due to significant exchanges of groundwater.

3.1.5 *C. carpio* dominance in Lake Naivasha

The fish community in Lake Naivasha is under pressure from over-fishing, decreasing water levels, changes in aquatic macrophyte densities and inadequate species diversity (Hickley *et al.*, 2002) since the discovery of the common carp, *Cyprinus carpio* L.. The carp *C. carpio* is a species that has been extensively translocated around the world and is generally considered an exotic pest (Sivakumaran *et al.*, 2003). Since its alien introduction in 1999, when *C. carpio* juveniles escaped during a flood at an on-line aquaculture site in the catchment and were washed into the lake, the first report of carp in the lake occurred in March 2001 and subsequently in commercial fishery catches in the year 2002 (Hickley *et al.*, 2004). Historically, commercial fishery of Lake Naivasha has been the subject of considerable fluctuations in catch rates, particularly of *O. leucostictus* (Figure 3). In recent years, catches of *M. salmoides* in both the

commercial fishery and the annual samples have decreased markedly and remain at extremely low levels (Figure 3). Although the first recording of *C. carpio* in the fishery was in March 2002, they initially remained only a minor component of total catch compared with both tilapia species. At the start of 2004, however, there was a marked shift in catches from tilapia to *C. carpio* and since this time, catches have generally comprised >90% carp (Figure 3). Between October 2005 and March 2006, the total mass of carp landed was 5511 kg, equivalent to 370 kg/ha (Britton *et al.*, 2007).

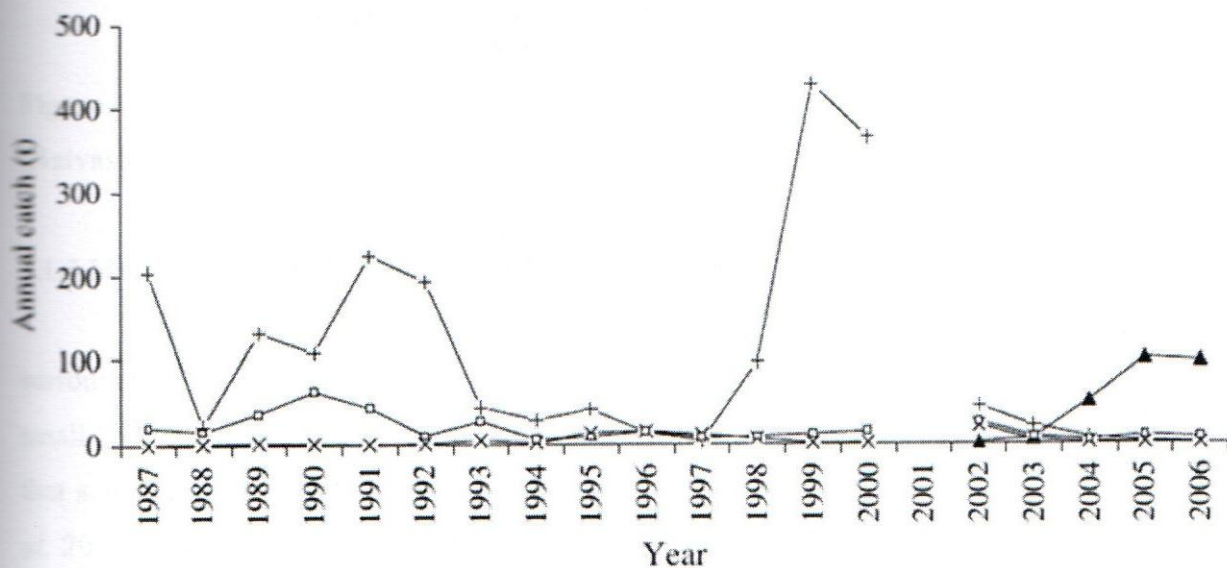


Figure 3: Composition of annual catches in Lake Naivasha of *Tilapia zillii* (X), *Oreochromis leucostictus* (+), *Micropterus salmoides* (□) and *Cyprinus carpio* (▲) (Britton *et al.*, 2007).

Further in the year 2008 the Naivasha Fisheries Station annual report (2008) indicated the dominance of common carp (*Cyprinus carpio*) at 89% followed by 'Lake Naivasha tilapia' (*Oreochromis leucostictus*) at 7%. The Mirror carp and Black bass (*Micropterus salmoides*) catches were recorded at 3% and 1% respectively (Figure 4).

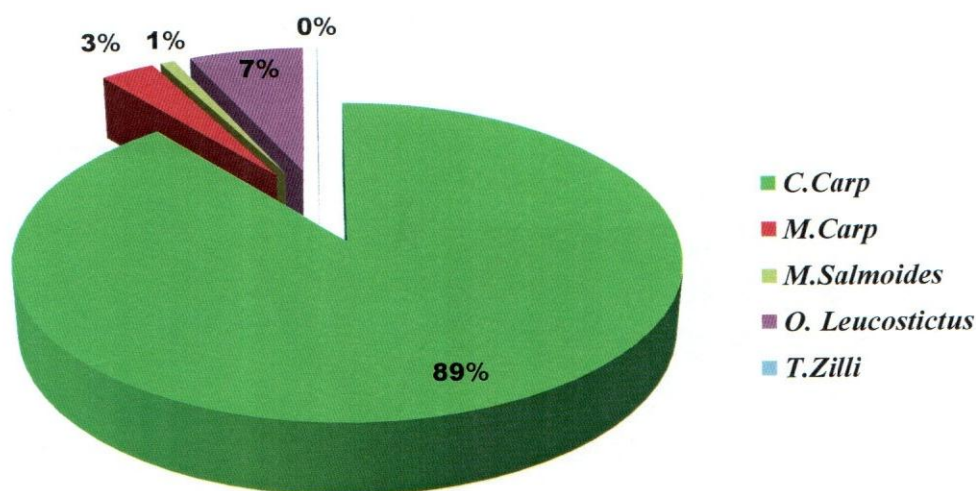


Figure 4: Percentage fish catches per species by weight in Lake Naivasha in the year 2008 (Naivasha fisheries station annual report, 2008)

3.1.5 Major human activities around Lake Naivasha

Social and economic activities dominate the Lake ecosystem and its entire catchment. Its surroundings support an intensively irrigated agricultural land (Figure 5) ranging from rural small holder farmers in the upper catchment and high value commercial exported horticulture that supports almost 650,000 people, a fast-growing township and industries (Otiang'a-Owiti *et al.*, 2007). North of the Lake is irrigated lucerne used as fodder for dairy cows since 1940s and North West (between Nakuru and Naivasha) cattle and game rangeland dominate. Open rangelands are south of the Lake where the Maasai graze their livestock during the dry season. Closer to the Lake edge occur many irrigated floriculture ventures whilst the areas to the west and east are dominated by small holders growing maize, vegetables and pyrethrum (Becht *et al.*, 2005). Larger grain farms also exist.

According to Otiang'a-Owiti and Oswe (2007) human activities driven by numerous stakeholders around the lake are the cause of serious impacts which include water pollution, inter-basin water transfer, water abstraction from the lake and from inflowing rivers, forest destruction in the catchment, siltation of the lake and inflowing rivers, habitat destruction, lake level and surface area recession, decline in fisheries resources and water bird populations, introduction of alien species of plants and animals, and the destruction of fringing papyrus beds. Most of these impacts have resulted in the destruction of the riparian/littoral zone around the lake

shore, one of the most important portions of the lake system (as a habitat for wildlife) which provides a natural filtration system for surface water run-off that enters the lake.

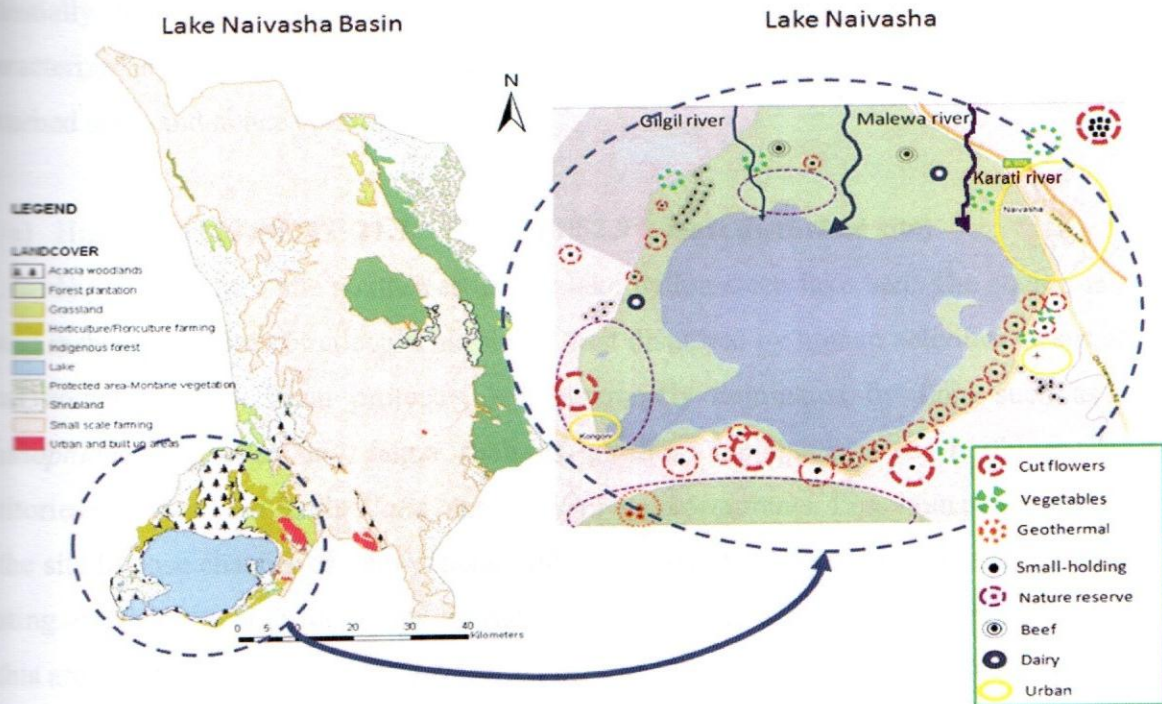


Figure 5: Socio-economic activities surrounding Lake Naivasha (modified from WWF, 2010)

3.2 Sampling sites

The sampling sites (Figure 2) were purposively chosen based on the possible routes of heavy metal pollutant entry into the lake whereas undisturbed areas served as control. Seven sampling sites (Hippo point, Kasarani, Mouth of Malewa, Mouth of Karati, Crescent Island, Sher Karuturi discharge outlet and Oserian discharge outlet) were purposively selected in Lake Naivasha, geo-referenced (using a handheld Global Positioning System (GPS), Garmin 12XL) and coded, out of which two sampling sites served as control sites in the study. Areas with intensive agricultural activities and wetland discharge outlets around the Lake represented disturbed areas due to the potent influx of contaminants into the aquatic ecosystem. Two chosen sites represented the floriculture industry which forms the major agricultural activity around the lake and included Sher Karuturi, Kasarani and Oserian discharge outlet. Mouths of rivers Malewa and Karati served as principal sample sites representing upstream anthropogenic

activities and possible contamination as they channel surface water into the Lake. In their course downstream, many small scale farmers tap the two rivers for water in their farms and could potentially contaminate their quality from use of agrochemicals. Hippo point and Crescent Island characterized by minimal anthropogenic activities; mostly boating and fishing served as least disturbed areas and hence control sites.

a) Hippo point (S 00° 47' 21.7'', E 36° 18'52.9''; **least disturbed site**)

Hippo point is a site south west of the lake with a steep lake bed. The station is a well-mixed inshore site about 6m deep. This site is least disturbed by human activities as surrounding areas comprise of personal protected habitats mostly dominated by flora such as *Acacia xanthophloea*, fig trees and fauna such as giraffes, hippopotamuses, buffaloes, avifauna territories (African Fish Eagle *Haliaeetus vocifer*) and cormorants. Less human activities prevail in the site to pose chances of heavy metal pollution. Commonly noted in this area is fishing and boating activities by both locals and tourists in the Lake Naivasha. The occurrence of *C. carpio* in this area is quite limited due to the clear undisturbed waters (Transparency 34 m) which do not favour its ecology as it thrives best in shallow sediment waters due to its benthivorous feeding characteristics.

b) Kasarani (S 00° 43' 22.7'', E 36° 18'40.3'' **flower farm discharge outlet**)

Kasarani site is an inshore area about 4m deep away from any inflow and situated northwest of the lake with minimal direct influence of both rivers and human activities such as farming. Several small scale flower farms (for example; Bila shaka, Aquilla and Shalimar flower farms) also surround the area having wetland discharge outlets into the Lake. Based on the agrochemicals in use; heavy metals are potential contents (Alloway and Aynes, 1993) which could have significant eco-toxicological effects in Lake Naivasha ecosystem if unchecked. The site is however swampy and dominated by papyrus (*Cyperus papyrus*) and water hyacinth (*Eichhornia crassipes*) plants. Avifauna such as the great white and pink backed pelicans, African fish eagle, coots, African darter, herons, ducks, grebes and other waders were seen floating on the hyacinth. The numerous abundance of wader birds noted here is an indicator of abundance of fish (particularly *C. carpio*).

c) Mouth of Malewa (S 00° 43' 44.0'', E 36° 20'45.4''; surface inflow)

This site represents a shallow turbid area having a depth of 2m where river Malewa enters Lake Naivasha. It represents Lake Naivasha's main surface inflow estimated at an annual flow of 153 million m³ and a maximum horizontal channel length of 109 km (Everard *et al.*, 2002) in a 1600 km² basin. The Malewa river system is significantly more dendritic than other systems in the catchment, with headwaters and tributaries rising at a range of altitudes. The headwater of the main channel of the Malewa River rises in the Nyandarua Mountains at 3700 m altitude and discharges directly into Lake Naivasha with no dissipation into papyrus swamps. Everard *et al.*, (2002) illustrated that the distinct sediment-plumes of the Malewa river water were visible up to 500 m in 1997 more so attributed to catchment activities. This has been due to extensive riparian land use at the Malewa catchment that includes tillage of the land for subsistence agriculture and cash crops whose impact is extensive erosion and agrochemical deposition into Lake Naivasha. *C. carpio* are known to best thrive in this waters (Muchai Fisheries department personal communication; 2010).

d) Mouth of Karati (S 00° 44' 15.3'', E 36° 23'04.3''; surface inflow)

Mouth of Karati site is shallow and turbid with a depth of approximately 1m depth. It represents the point at which river Karati enters Lake Naivasha. During the entire sampling period (March to May), the river was flowing intermittently into Lake Naivasha. The Karati River is a relatively shorter, steeper system with no significant tributaries straddling a maximum horizontal channel length of about 30 km within a 150 km² basin (Lukman, 2003). The headwater rises at an altitude of 2600 m on the Kinangop plateau, but cascades steeply from the Rift Valley edge towards the flatter lands bordering the eastern lake shore. Subsistence agriculture and cash crop are evident in the Kinangop plateau which could be the reason for the observed sediment depositions at the river mouth hence the possibility of contaminated inflows. Hippopotamuses are also quite evident in this site. Avifauna and vegetation abundance is quite ample; a visual indicator of aquatic life abundance especially *C. carpio*.

e) Crescent Island Lake (S 00° 44' 43.6'', E 36° 24'12.4''least disturbed site)

The site lies east of the Main Lake with an almost enclosed sub-basin at 18 m depth having minimal interactions from the main lake. The only major human activities evident in this

area are fishing and boating. The waters are clear, cool and calm with benthivorous fish (particularly *C. carpio*) found at greater depths below. Avifauna abundance is also quite evident especially great white and pink backed pelicans, cormorants and herons; an indication of rich aquatic life.

f) Sher Karuturi (S 00° 49' 10.2'', E 36° 21' 29.4'' flower farm discharge outlet)

Sher Karuturi sampling station lies to the Southwest of the lake having a depth of approximately 2m. The station is a wetland discharge outlet of a large international exporter; Sher Karuturi flower farm. The water is highly turbid and often brown in colour due to suspended sediments. Intensive large scale floricultural farming takes place in the riparian land making use of agrochemicals. The agrochemicals are suspected to contain traces of heavy metals (Gitahi, 2002). Many locals were also observed putting up fishing nets at this end; discussions with them revealed that this after the Malewa River mouth was a good spot for *C. carpio* fishing.

g) Oserian (S 00° 48' 37.1'', E 36° 17' 47.5'' flower farm discharge outlet)

Oserian discharge outlet has a depth of approximately 2m. The discharge outlet serves one of the largest flower farm producer and international exporter in East Africa; the Oserian flower farm. The water is relatively turbid. Heavy metals are suspected as active ingredients of the agrochemicals (Gitahi, 2002) used and discharged by the flower farm in the area. The area is highly invaded by hippopotamuses and flora; the water hyacinth (*Eichhornia crassipes*) and papyrus (*Cyperus papyrus*).

3.3 Assessment of Cu, Pb and Cd concentrations in Lake Naivasha

Samples were randomly collected in triplicates from seven sampling sites along Hippo point, Kasarani, Mouth of Malewa, Mouth of Karati, Crescent Lake, Sher Karuturi and Oserian discharge outlets. Three replicates of water and sediments were randomly collected four times in March (once), April (once) and May (twice) from each of the selected sampling sites. A total of 84 *C. carpio* were assayed.

3.3.1 Limnological parameters

Knowledge of limnological parameters of natural waters is pertinent because these parameters can modify toxicities of various heavy metals and therefore indicate the water quality of the ecosystems (Ochieng *et al.*, 2007). Low pH (Acidic), high temperatures, low light transparency, low dissolved oxygen concentration and high total dissolved solids and electrical conductivity will alter metal speciation, solubility and availability and increase their respective toxicities (Adefemi and Awokunmi, 2010).

pH, temperature, light transparency, water conductivity, total dissolved solids, and dissolved oxygen were measured *in situ* from each sampling station three times during every sampling period (March to May 2010). A Hydro lab YSI model 85 was used to measure pH, Temperature ($^{\circ}\text{C}$), water conductivity ($\mu\text{S cm}^{-1}$), total dissolved solids (mgL^{-1}) and dissolved oxygen (mgL^{-1}). A secchi disc was used to measure light transparency. Three readings of each environmental variable were taken from each site and thereafter the average determined to ensure accuracy of the equipment (Okalebo and Gathua, 1993).

3.3.2 Water and sediment sampling

Teflon sampling bottles were pre-cleaned thoroughly with detergent, and soaked overnight in 6 % nitric acid and thereafter rinsed with distilled water. These were then stored in a dust free place to avoid contamination. In the lake, water sampling was conducted in triplicates in each of the seven sampling sites. A sample of 500 ml of water was taken by immersing the bottles and lifting them up. 4ml of 2 % nitric acid was then added to the water samples to adjust the pH and maintain the heavy metals in solution. In the laboratory, the water samples were filtered, to 100 ml pre-cleaned plastic bottles through 0.45 μm Millipore filter papers (Whatman no. 42) to remove any suspended organic materials and further prevent microbial growth, flocculation and adsorption on container surfaces. The water samples were then stored at 4°C in the refrigerator to await analysis using the Atomic Absorption Spectrometer; Thermo Jarrell Ash aa/ae spectrophotometer S11 equipment.

Bottom sediment samples were taken from the sites in triplicates using a stainless steel Ekman grab sampler and stored in Teflon polythene bags to avoid contamination. These were then transported to the laboratory for further processing. In the laboratory, samples were dried in the oven overnight at 110°C ; these were then crushed in a mortar and pestle and sieved using a 2

mm mesh sieve to remove plant parts and debris. One gram (dry weight) portions were then weighed using an analytical balance to digestion tubes. A digestion mixture was prepared containing 0.42 g selenium powder (catalyst), 14 g lithium sulphate, 350 ml hydrogen peroxide and 420 ml sulphuric acid in an ice bath (Okalebo and Gathua, 1993). 5mls of the digestion mixture were then added to the one gram dry weight sediment portions in the digestion tubes and digested in a digestion block for 2 hours at 360°C until clear solutions were obtained. Digests were then left to cool to ambient temperatures (25°C). The resulting solutions were then filtered using 0.45 µm Millipore filter papers (Whatman no. 42) and volume topped to 100 ml using distilled de-ionized water. Thereafter, the digests were stored in the refrigerator at 4°C in pre-cleaned plastic bottles before analysis using the Atomic Absorption Spectrometer; Thermo Jarrell Ash aa/ae spectrophotometer S11 equipment.

3.3.3 *Cyprinus carpio* Sampling

Freshly caught *C. carpio* were bought from local fishermen who were fishing at the different sampling sites, placed in a cool box and taken to the laboratory for further processing of the samples. Kenya Marine and Fisheries Research Institute (KEMFRI) were consulted in the field for purposes of *C. carpio* identification. In the Laboratory, *C. carpio* samples were washed with distilled water and scales removed. Only tissues without bone were selected for extraction. Two portions of 10 cm² of wet fish muscle were cut and homogenized in a pestle and mortar. 2 g wet weight, (WW) portions were then taken from each sample into a digestion tube and digested using a 10 ml prepared digestion mixture (0.42 g selenium powder (catalyst), 14 g lithium sulphate, 350 ml hydrogen peroxide and 420 ml sulphuric acid) in a digestion block for 2 hours at 360°C until clear solutions were realized (Okalebo and Gathua, 1993). The resulting solutions were filtered using 0.45 µm Millipore filter papers (Whatman no. 42) and volume topped to 100 ml using distilled de-ionized water. The digests were then stored in the refrigerator at 4°C in pre-cleaned plastic bottles before analysis using Atomic Absorption Spectrometer ; Thermo Jarrell Ash aa/ae spectrophotometer S11 equipment.

3.3.4 Atomic Absorption Spectrometer (AAS)

Atomic Absorption Spectrometer Thermo Jarrell Ash aa/ae spectrophotometer S11 equipment was used in the analysis of copper, lead and cadmium concentrations from the

water, sediment and *C. carpio* muscle tissues prepared in the laboratory. The detection limits for the AAS analysis in sediments and *C. carpio* muscle tissues was Pb 0.1 ppm, Cd 0.01 ppm and Cu 0.03 ppm while for water; Pb – 100 ppb, Cu – 30 ppb and Cd – 10 ppb respectively. All sample preparations and analysis were carried out using standard methods of analysis (Radojevic and Bashkin, 1999). The concentrations of the metals were assayed in triplicates by use of an AAS with acetylene flame (the accuracy of the instrument was checked by triplication of samples). A series of standards were prepared for instrumental calibration by serial dilution of a working solution (100 ppm) prepared from analytical grade stock solutions (1000 ppm) from BDH Poole and Sigma Aldrich. A standard and blank sample was run after every seven samples to check instrumental drift. Calibration curve method was used to quantify the heavy metal concentrations.

3.4 Data Analysis

The data was analyzed using the Statistical Package for Social Sciences (SPSS® Version 17 for Windows). Descriptive statistics was used to summarize the concentration of heavy metals in sediments, water and *C. carpio* muscle tissues as arithmetic mean with standard deviation (mean $\pm$ standard deviation). Before applying the parametric tests, the data was tested for homogeneity of variances using F-max test (Sokal and Rohlf, 1995). This test is meant to decide if the difference between two or more sample variances is so small that it may be ignored. The data that did not meet this assumption was transformed as $\log_{10}(x+1)$. One way analysis of variance (ANOVA) was applied to test the differences of mean heavy concentration in water, sediments and *C. carpio* muscle tissues between sampling sites. Least Significant Difference test (LSD, $\alpha = 0.05$) was applied for pairwise comparison of mean concentrations between sites whenever analysis of variance resulted to significant F-values. A paired t-test was further used to analyze the differences in the means of Cd, Cu and Pb concentration in the sediments, water and *C. carpio* muscle tissues with the recommended limits. To explore the variation of heavy metal concentrations in sediment, water, *C. carpio* muscle tissue samples and sampling sites in Lake Naivasha; Two way ANOVA was used. The two-way ANOVA is appropriate because it is able to test the differences in the means when there are more than two independent variables. In this case each metal concentration was analysed with regards to the matrix and the sampling site. All statistical analyses were tested at 0.05 significance level (Sokal and Rohlf, 1995).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1.1 Limnological parameters

Water quality parameters are presented as arithmetic mean $\pm$ standard deviation (Table 1). Data shown is the average of four measurements taken from each of the seven sampling sites.

Table 1: Water physical chemical parameters obtained during sampling in Lake Naivasha

Site	pH	Temp (°C)	Trans (cm)	Cond (μScm^{-1})	TDS (mg L^{-1})	DO (mg L^{-1})
Hippo point	8.5 ± 0.9	23.5 ± 1.7	34	354.5 ± 21.9	175.5 ± 21.9	6.4 ± 0.3
Kasarani	7.8 ± 0.6	22.3 ± 0.4	28	344.5 ± 7.7	171.5 ± 12.0	5.2 ± 1.6
Mouth of Malewa	8.7 ± 1.1	23.2 ± 2.9	24	343.0 ± 15.5	170.0 ± 8.4	6.5 ± 1.8
Mouth of Karati	8.5 ± 0.7	23.4 ± 1.4	26	339.0 ± 12.7	169.5 ± 6.4	6.4 ± 1.2
Crescent Island	8.6 ± 0.3	23.7 ± 1.2	55	373.0 ± 16.9	187.5 ± 6.4	6.5 ± 0.7
Sher Karuturi	7.8 ± 0.9	22.5 ± 1.2	25	346.0 ± 14.1	162.0 ± 2.8	6.5 ± 0.7
Oserian outlet	8.9 ± 0.7	23.7 ± 2.3	26	369.5 ± 34.6	181.0 ± 15.5	6.8 ± 0.8
LN No. 120 (2006)	6.5 - 8.5	30.0			1200	
WHO, 1984, 2008	6.5 - 8.5			1500	1000	4.5 - 7.5

Temp Temperature, Trans Transparency, Cond Conductivity, TDS Total Dissolved Solids, DO Dissolved Oxygen, LN Legal Notice No. 120 (water quality regulations in Kenya), WHO World Health Organization Desirable Levels

The pH of surface water measured from various sampling stations ranged from 7.8 – 8.9. The highest pH value of 8.9 was recorded at Oserian discharge outlet which was the most alkaline. The lowest pH value recorded was 7.8 for both Kasarani and Sher Karuturi discharge outlets which was slightly above the normal neutral value of 7.0. The measured temperatures of water from the different stations ranged between 22.3 – 23.7 °C with the highest at Oserian discharge outlet and Crescent Island (23.7 °C) and the lowest at Kasarani area (22.3°C). Light transparency was highest at Crescent Island (55 cm) and lowest at Mouth of Malewa (24 cm). The conductivity values of stations with anthropogenic influence that is Kasarani, Mouths of Malewa and Karati, Sher Karuturi and Oserian discharge outlets ranged from 339 – 369.5 $\mu\text{S/cm}$ while for least disturbed sites was 354.5 $\mu\text{S/cm}$ at Hippo point and 373 $\mu\text{S/cm}$ at Crescent Island. The TDS values ranged from 162.0 – 187.5 mg/L with the highest value recorded at Crescent Island and lowest at Sher Karuturi discharge outlet. The dissolved oxygen concentration was the highest at Oserian discharge outlet (6.8 mg/L). All the stations recorded dissolved oxygen

concentrations between 6.4 and 6.8 mg/L except for Kasarani whose concentration was the lowest at 5.2 mg/L.

Comparing this data with other researchers and especially Were (2007), a pH value of 8.7, temperatures of 25.1°C, Conductivity of 325 μ S/cm, TDS of 162 mg/L and DO values of 1.2 mg/L were obtained in Lake Naivasha. The parameters remain within recommended levels however with notably variable DO levels which could be due to the high recorded temperatures (25.1°C) contrary to 23.7°C in this study. Warmer water will tend to hold less oxygen than cooler water. The pH tends to alkalinity slightly above neutral due to the fact that Lake Naivasha is volcanic, rich in carbonates and bicarbonates derived from the carbonatite volcanic rocks. The closed seepage nature of Lake Naivasha contributes to its freshness and thus low TDS (< 1000 mg/L) and conductivity (< 1500 μ S/cm) values in all the sites. TDS and conductivity values show slight variation among the sites due to changes in electrolyte concentrations and assimilation by aquatic biota (Ochieng *et al.*, 2007). Dissolved oxygen concentration changes are in principle highly attributed to temperature, depth and ecological processes in the lake and more so pH. The pH values tending toward alkaline render loss of ions and especially free CO₂ ions which is matched by an increase in DO, for example Oserian discharge outlet exhibited the highest pH value of 8.9 and a DO of 6.8 mg/L compared to the other sites while the vice versa is true for Kasarani. Kasarani exhibits slightly lower DO levels of 5.2 mg/L and pH value of 7.8. Light transparency (secchi depth) levels were variable among the sites and especially the shallow sites; Kasarani 28 cm, Mouth of Malewa 25 cm, Mouth of Karati 26 cm, Sher Karuturi 25 cm and Oserian outlet 26 cm which could be attributed to effluent inflow and turbulence that stir the shallow turbid waters. Hippo point recorded a secchi depth of 34 cm while Crescent Island 55 cm. Inferred from this is that there could be deposition inflows from the shallow sites with low secchi depth (range 25 – 28 cm). This is explained by the fact that the 2 river inlets deposit a lot of sediment and nutrient material from the catchment (Tarras-Wahlberg *et al.*, 2002; Otiang'ao-Owiti, *et al.*, 2007), whilst Kasarani, Sher Karuturi and Oserian are significant flower farm effluent discharge outlets. Significant inflows from the sites render the water turbid and thus low secchi depths. Hippo point and Crescent Island marked by high secchi depths depict less turbid and reasonably clear waters; the explanation that there is less intrusion by turbid material.

In general, *in situ* parameters of pH, temperature, light transparency and dissolved oxygen in all the sampling sites were in compliance with the defined Kenyan guide values (maximum permissible) for sources of domestic water and WHO drinking standards (Table 1). pH was the only parameter with exceptions where Mouth of Malewa (8.7), Crescent Island (8.6) and Oserian discharge outlets (8.9) were slightly above the Kenya (Legal Notice No. 120, 2006) and WHO (1984, 2008) required range of 6.5 – 8.5. The impact however on heavy metal would be of less toxicity as metals tend to be more toxic at lower pH because they become more soluble (Gibbons *et al*, 1994).

4.2 Heavy metal concentrations in sediments

Three heavy metals namely, Cadmium (Cd), Copper (Cu) and Lead (Pb) were considered in this study. The specific analyses are presented in the preceding sections.

4.2.1 Cadmium Concentration in sediments

The cadmium concentration values among the sites ranged between 1.2 – 5.4 mg/kg. Hippo point, Kasarani, Mouth of Malewa and Sher Karuturi sampling sites recorded a range from 2.1 – 2.7 mg/kg while 3.3 mg/kg was recorded at Mouth of Karati (Table 2).

Table 2: Cadmium concentration (mg/kg) in sediments between March and May 2010

Sampling Station	Mean concentration $\pm$ STDEV
Hippo point	2.1 $\pm$ 0.2
Kasarani	2.2 $\pm$ 0.1
Mouth of. Malewa	2.7 $\pm$ 1.3
Mouth of Karati	3.3 $\pm$ 1.0
Crescent Island	1.2 $\pm$ 0.3
Sher Karuturi	2.4 $\pm$ 1.5
Oserian	5.4 $\pm$ 0.7

STDEV Standard Deviation

Oserian discharge outlet had the highest cadmium concentration of 5.4 mg/kg while Crescent Island (1.2 mg/kg) and Hippo point (2.1 mg/kg) sediments recorded low concentrations.

To establish if there was a significant difference in the means of the Cadmium concentration in sediments among the various study stations, ANOVA was performed (Appendix D). The results indicate that there was a significant difference ($p = 0.000$) in the means of Cadmium concentration between the sampling sites at 5% significance level. This implies that some locations have higher Cadmium concentrations (Oserian at 5.4 mg/kg) in sediments than others (Hippo point at 1.2 mg/kg). Since the ANOVA revealed that there was a significant difference in the means of Cadmium concentrations in the different sample stations in the sediments, it was important to find out where these differences occur. Post hoc test; the Least Significance Difference (LSD) was employed for this purpose. The procedure revealed that the differences in the mean Cadmium concentrations within the sediments were significant for the following pairs of sites shown in Table 3.

Table 3: LSD for Cadmium Concentration in sediments among the different sample stations in Lake Naivasha.

(I) Sample station	(J) Location	Mean Difference (I-J)	Significance
Hippo point	Oserian	-3.3*	0.000
Kasarani	Oserian	-3.2*	0.000
Mouth of Malewa	Crescent Island	1.6*	0.022
Mouth of Malewa	Oserian	-2.6*	0.000
Mouth of Karati	Crescent Island	2.1*	0.003
Sher Karuturi	Oserian	-2.9*	0.000

* Significant ($P < 0.05$)

4.2.2 Copper Concentration in sediments

The copper concentrations in sediments are presented in Table 4 below.

Table 4: Copper concentration (mg/kg) in sediments between March and May 2010

Sampling station	Mean concentration $\pm$ STDEV
Hippo point	3.0 ± 0.0
Kasarani	8.2 ± 0.4
Mouth of Malewa	8.4 ± 1.7
Mouth of Karati	3.6 ± 0.2
Crescent Island	3.0 ± 0.0
Sher Karuturi	5.8 ± 0.8
Oserian	6.3 ± 0.2

STDEV Standard Deviation

Concentration of copper in sediments ranged from 3.0 to 8.4 mg/kg among the sites .In decreasing copper concentration order, Mouth of Malewa recorded the highest copper concentration of 8.4 mg/kg, Kasarani 8.2 mg/kg, Oserian discharge outlet 6.3 mg/kg, Sher Karuturi 5.8 mg/kg, Mouth of Karati 3.6 mg/kg, Crescent Island 3.0 mg/kg and Hippo point at 3.0 mg/kg.

One away ANOVA indicated a significant difference ($p = 0.000$) in the mean concentrations between the various sampling stations in the sediments at 5% significance level (Appendix I). Table 5 shows further post hoc test, LSD for pairs of sites where the differences in the mean Copper concentrations occurred within the sediments.

Table 5: LSD for Copper concentrations in sediments among the different sample stations in Lake Naivasha.

(I) Sampling stations	(J) Sampling stations	Mean Difference (I-J)	Sig.
Hippo point	Kasarani	-5.2*	0.000
Hippo point	Mouth of Malewa	-5.5*	0.000
Hippo point	Sher Karuturi	-2.9*	0.000
Hippo point	Oserian	-3.4*	0.000
Kasarani	Hippo	5.2*	0.000
Kasarani	Mouth of Karati	4.6*	0.000
Kasarani	Crescent Island	5.2*	0.000
Kasarani	Sher Karuturi	2.4*	0.000
Kasarani	Oserian	1.9*	0.002
Mouth of Malewa	Mouth of Karati	4.8*	0.000
Mouth of Malewa	Crescent Island	5.5*	0.000
Mouth of Malewa	Sher Karuturi	2.6*	0.000
Mouth of Malewa	Oserian	2.1*	0.001
Crescent Island	Sher Karuturi	-2.9*	0.000
Crescent Island	Oserian	-3.4*	0.000
Sher Karuturi	Mouth of Karati	2.2*	0.001

* Significant ($P < 0.05$)

4.2.3 Lead Concentration in sediments

The range of mean lead concentrations in the sediments ranged from 17.1 – 53 mg/kg (Table 6) among the sites. The lowest mean lead concentration in sediments 17.1 mg/kg was recorded at Hippo point with the highest 53.1 mg/kg at Mouth of Malewa.

Table 6: Lead concentration (mg/kg) in sediments between March and May 2010

Sampling Station	Mean concentration $\pm$ STDEV
Hippo point	17.1 $\pm$ 5.4
Kasarani	26.8 $\pm$ 1.5
Mouth of Malewa	53.1 $\pm$ 3.6
Mouth of Karati	47.4 $\pm$ 3.5
Crescent Island	20.5 $\pm$ 1.1
Sher Karuturi	34.2 $\pm$ 1.9
Oserian	36.8 $\pm$ 3.9

STDEV Standard Deviation

One way ANOVA revealed that the mean differences are statistically significant ($p = 0.000$) at 5% significant level (Appendix I). Post hoc test LSD identified significant differences in the mean lead concentrations within the sediments for the following pairs of sites shown in Table 7.

Table 7: LSD for Lead concentrations in sediments among the different sample stations in Lake Naivasha.

(I) Sampling stations	(J) Sampling stations	Mean Difference (I-J)	Significance
Hippo point	Kasarani	-9.6*	0.001
Hippo point	Mouth of Malewa	-35.9*	0.000
Hippo point	Mouth of Karati	-30.3*	0.000
Hippo point	Sher Karuturi	-17.1*	0.000
Hippo point	Oserian	-19.7*	0.000
Kasarani	Mouth of Malewa	-26.3*	0.000
Kasarani	Mouth of Karati	-20.6*	0.000
Kasarani	Crescent Island	6.3*	0.014
Kasarani	Sher Karuturi	-7.5*	0.005
Kasarani	Oserian	-10.1*	0.000
Mouth of Malewa	Mouth of Karati	5.7*	0.025
Mouth of Malewa	Crescent Island	32.6*	0.000
Mouth of Malewa	Sher Karuturi	18.9*	0.000
Mouth of Malewa	Oserian	16.2*	0.000
Mouth of Karati	Hippo point	30.3*	0.000
Mouth of Karati	Crescent Island	26.9*	0.000
Mouth of Karati	Sher Karuturi	13.2*	0.000
Mouth of Karati	Oserian	10.5*	0.000
Crescent Island	Sher Karuturi	-13.7*	0.000
Crescent Island	Oserian	-16.4*	0.000
Sher Karuturi	Hippo point	17.2*	0.000
Oserian	Hippo point	19.7*	0.000

* Significant ($P < 0.05$)

4.2.4 Cd, Cu and Pb concentrations in sediments and comparison with recommended limits

The highest lead (53.1 mg/kg) and copper content (8.4 mg/kg) is found in sediments from the mouth of River Malewa which could be due to the flow of contaminated sediments from the catchment. Cadmium concentration in all the sites was above the cadmium sediment quality guidelines of NOAA 0.6 mg/kg LEL (Lowest Effect Level) and 0.99 mg/kg TEC (Threshold Concentration) recommended limits but below the NOAA Severe Effect Level (SEL) of 10.0 mg/kg. Copper concentration among the seven sites was below the NOAA 16.0 mg/kg LEL, 31.6 mg/kg TEC and 110.0 mg/kg SEL copper sediment quality guidelines. Hippo point, Kasarani and Crescent Island sampling stations recorded lead concentrations below the NOAA 16.0 mg/kg LEL, 31.6 mg/kg TEC and 110.0 mg/kg SEL Lead sediment quality guidelines, other stations recorded values above the recommended limits (Table 8).

Table 8: Cadmium, copper and lead concentration in the Lake Naivasha sediment and comparison with the NOAA (2009) Sediment Quality Guidelines

Sampling Station	Mean concentration $\pm$ Standard deviation		
	Cadmium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)
Hippo point	2.1 $\pm$ 0.2	3.0 $\pm$ 0.0	17.1 $\pm$ 5.4
Kasarani	2.2 $\pm$ 0.1	8.2 $\pm$ 0.4	26.8 $\pm$ 1.5
Mouth of Malewa	2.7 $\pm$ 1.3	8.4 $\pm$ 1.7	53.1 $\pm$ 3.6
Mouth of Karati	3.3 $\pm$ 1.0	3.6 $\pm$ 0.2	47.4 $\pm$ 3.5
Crescent Island	1.2 $\pm$ 0.3	3.0 $\pm$ 0.0	20.5 $\pm$ 1.1
Sher Karuturi	2.4 $\pm$ 1.5	5.8 $\pm$ 0.8	34.2 $\pm$ 1.9
Oserian	5.4 $\pm$ 0.7	6.3 $\pm$ 0.2	36.8 $\pm$ 3.9
Recommended Limit in mg/kg (NOAA, 2009)			
LEL	0.6	16.0	31.0
TEC	0.99	31.6	35.8
SEL	10.0	110.0	250.0

LEL National Oceanic and Atmospheric Administration (NOAA, 2009) Lowest Effect Level in sediments, *TEC* NOAA Threshold Effect Concentration in sediments, *SEL* NOAA Severe Effect Level in sediments

A paired t-test was further used to analyze the differences in the means of Cd, Cu and Pb concentration in the sediments with the recommended limits. Results (Table 9) indicated a significant difference between the mean concentrations for Cd, Cu and all the recommended values. The difference is also significant for Pb and SEL. However, for Pb and LEL, Pb and TEC, there is no statistically significant difference at 5% significance level ($p = 0.281$, $p = 0.395$).

Table 9: T-test for Cd, Cu and Pb in the sediments with the recommended limits

Heavy Metal – Recommended limits	Mean		
	difference	t-statistic	P-value
Cd concentration (mg/kg) - LEL	2.148	7.702*	0.000
Cd concentration (mg/kg) - TEC	1.758	6.304*	0.000
Cd concentration (mg/kg) - SEL	-7.251	-25.999*	0.000
Cu Concentration (mg/kg) - LEL	-10.489	-23.999*	0.000
Cu Concentration (mg/kg) - TEC	-26.089	-59.689*	0.000
Cu Concentration (mg/kg) - SEL	-104.489	-239.054*	0.000
Pb Concentration (mg/kg) - LEL	2.688	1.100	0.281
Pb Concentration (mg/kg) - TEC	-2.111	-0.864	0.395
Pb Concentration (mg/kg) - SEL	-216.311	-88.493*	0.000

* Significant ($P < 0.05$)

Of the three metals assessed, the data indicates that the concentration of cadmium in sediments is the least owing to probabilities of either low inflows of colloidal particulate

cadmium into the Lake or higher cadmium assimilation by the Lake biotic community. Furthermore, the form (gaseous, liquid or solid) in which heavy metals enter the aquatic system highly influences their bioavailability in sediments. Lead concentration on the other hand is the highest; this could be due to high leaded inflows which stream in as sediment loads or effluent (in agrochemicals) especially at the Mouths of Malewa and Karati, Sher Karuturi and Oserian discharge outlets. Copper concentration is lower than the recommended limits in sediments; the reason could be bio-assimilation as copper is an essential enzymatic component in a biological system (Kalay and Canli, 2000). Comparing the findings with other researchers; Tarras-Wahlberg *et al.*, (2002) reported high Cd concentrations of 7 and 6 mg/kg, Cu at 45 mg/kg and Pb at 20 mg/kg in Lake Naivasha sediments. Ochieng *et al.*, (2007) on the other hand reported lower Cd concentrations of 0.73 mg/kg, Cu 10.73 mg/kg and Pb at 25.34 mg/kg. The varying concentrations are largely attributed to assimilation by flora and fauna in the Lake and, use and release of chemical fertilizers into the Lake. According to Driver *et al.*, (1999) cadmium is a common contaminant of rock phosphorus, the major ingredient of chemical fertilizers. This explains the high cadmium concentration at the river mouth discharge area (Mouth of Malewa and Mouth of Karati) and flower farm discharge outlet (Kasarani, Sher Karuturi and Oserian). In his study, Gitahi *et al.*, (2002) further confirms that heavy metals especially Cu and Pb are active ingredients of pesticides contaminating Lake Naivasha which could be found in use as copper based fungicides and lead sprays. This therefore confirms the data findings on the abundance of lead and copper in sediments. Alloway and Aynes (1993), also indicate that Cd, Cu and Pb are to be found in composts and manure, which are activities taking place in farms around the Lake and its catchment. These heavy metals could be carried as runoff and discharged into the Lake.

The Crescent Lake has the lowest amount of cadmium, copper and lead in the sediments; this could be due to lack of discharge canals and other inflows in to the Lake. Hippo Point also has lower cadmium; copper and lead concentrations and this could be due to less pollution from human activities and chemical processes in addition to geochemical redistribution of existing natural cadmium, copper and lead concentration (Tarras-Wahlberg *et al.*, 2002).

Mouths of Malewa and Karati show high lead and cadmium concentrations beyond the NOAA guidelines, this could be attributed to the fact that they are key in sediment translocation

and deposition (containing heavy metals) into the lake as they originate from the catchment areas and form the major surface inflows into the lake. Activities around the catchment areas are mostly agricultural oriented using agro-chemicals with lead, copper and cadmium as ingredients which can attest to the changing metal load in the sediments. There is also a major highway above the Malewa Bridge that could also be a contributing factor to leaded vehicular emissions. The Sher Karuturi and Oserian flower farm discharge outlets showed significant lead and copper metal loads as well, this could be attributed to the agrochemicals use; however copper concentrations were below the LEL.

High metal inputs in aquatic ecosystems are therefore highly contributed by anthropogenic load as well as changes in geochemical processes, for example; in Baltic sea surface sediments; higher mean concentrations (in mg/kg) of Cd, Cu and Pb were reported and reasons given indicated influence by changes in redox potential and depleted oxygen as a result of organic and nutrient loads in the seawater (Borg and Jonsson, 1996).

4.3 Heavy metal concentrations in water

Cadmium (Cd), Copper (Cu) and Lead (Pb) concentrations in the water were analyzed using the AAS as presented below.

4.3.1 Cadmium concentration in water

Mean cadmium concentration in Lake Naivasha was quite low ranging from 10.0 $\mu\text{g/L}$ - 10.1 $\mu\text{g/L}$. Sher Karuturi discharge outlet had the highest concentration of 10.1 $\mu\text{g/L}$ while all the other stations recorded 10.0 $\mu\text{g/L}$ (Table 10).

Table 10: Cadmium concentration ($\mu\text{g/L}$ or ppb) in water between March and May 2010

Sampling station	Mean concentration $\pm$ STDEV
Hippo point	10.0 ± 0.0
Kasarani	10.0 ± 0.0
Mouth of Malewa	10.0 ± 0.0
Mouth of Karati	10.0 ± 0.0
Crescent Island	10.0 ± 0.0
Sher Karuturi	10.1 ± 0.1
Oserian	10.0 ± 0.0

STDEV Standard Deviation

The difference in the average Cadmium concentration in water in the various sampling stations is not statistically significant at 5% significance level ($p = 0.451$, See Appendix II). Since there was no significant difference in the Cadmium concentrations in water, the post hoc test mainly the LSD was not performed.

4.3.2 Copper concentration in water

The mean copper concentration in water was quite low. The highest mean copper concentrations $32.3 \mu\text{g/L}$ were recorded at Sher Karuturi while all the other stations recorded $30.0 \mu\text{g/L}$ (Table 11).

Table 11: Copper concentration ($\mu\text{g/L}$ or ppb) in water between March and May 2010

Sampling station	Mean concentration $\pm$ STDEV
Hippo point	30.0 ± 0.0
Kasarani	30.0 ± 0.0
Mouth of Malewa	30.0 ± 0.0
Mouth of Karati	30.0 ± 0.0
Crescent Island	30.0 ± 0.0
Sher Karuturi	32.3 ± 2.9
Oserian	30.0 ± 0.0

STDEV Standard Deviation

There was no significant difference ($p = 0.056$) in the means of the Copper concentrations in water at the different sampling stations (Appendix II).

4.3.3 Lead concentration in water

The highest mean lead concentrations in water were recorded at the river surface inflow sites; Mouth of Malewa $179.8 \mu\text{g/L}$ and Mouth of Karati $127.5 \mu\text{g/L}$ while the lowest was $100 \mu\text{g/L}$ at Hippo point, Kasarani and Crescent Island (Table 12).

Table 12: Lead concentration ($\mu\text{g/L}$ or ppb) in water between March and May 2010

Sampling stations	Mean concentration $\pm$ STDEV
Hippo point	100.0 $\pm$ 0.0
Kasarani	100.0 $\pm$ 0.0
Mouth of Malewa	179.8 $\pm$ 43.0
Mouth of Karati	127.5 $\pm$ 31.8
Crescent Island	100.0 $\pm$ 0.0
Sher Karuturi	108.6 $\pm$ 17.3
Oserian	108.6 $\pm$ 17.3

STDEV Standard Deviation

The difference in mean lead concentration at the different stations is statistically significant at 5% significance level ($p = 0.000$, Appendix II). Table 12 shows LSD results on pairs of sites where significant differences occurred.

Table 13: LSD for Lead concentration in water among the different sample stations in Lake Naivasha.

(I) Sampling stations	(J) Sampling stations	Mean Difference (I-J)	Significance
Hippo point	Mouth of Malewa	-79.8*	0.000
Kasarani	Mouth of Malewa	-79.8*	0.000
Mouth of Malewa	Hippo	79.8*	0.000
Mouth of Malewa	Kasarani	79.8*	0.000
Mouth of Malewa	Mouth of Karati	52.3*	0.003
Mouth of Malewa	Crescent Island	79.8*	0.000
Mouth of Malewa	Sher Karuturi	71.2*	0.000
Mouth of Malewa	Oserian	71.2*	0.000
Mouth of Karati	Hippo point	27.5	0.095
Mouth of Karati	Kasarani	27.5	0.095
Mouth of Karati	Mouth of Malewa	-52.3*	0.003

* Significant ($P < 0.05$)

4.3.4 Cd, Cu and Pb concentrations in water and comparison with recommended limits

The results indicate that lead is the most predominant detected only at the River mouths; Malewa and Karati and Sher Karuturi discharge outlet (Table 13); however the concentrations are in the $\mu\text{g/L}$ or ppb range. Copper and cadmium concentrations were only detected at the Sher discharge canal indicating significant inflows from the flower farm.

Table 14: Cadmium, Copper and Lead concentration in the Lake Naivasha water and comparison with Water Quality Guidelines

Sampling Station	Mean concentration $\pm$ Standard deviation		
	Cadmium ($\mu\text{g/l}$)	Copper ($\mu\text{g/l}$)	Lead ($\mu\text{g/l}$)
Hippo point	10.0 $\pm$ 0.0	30.0 $\pm$ 0.0	100.0 $\pm$ 0.0
Kasarani	10.0 $\pm$ 0.0	30.0 $\pm$ 0.0	100.0 $\pm$ 0.0
Mouth of Malewa	10.0 $\pm$ 0.0	30.0 $\pm$ 0.0	179.8 $\pm$ 43.0
Mouth of Karati	10.0 $\pm$ 0.0	30.0 $\pm$ 0.0	127.5 $\pm$ 31.8
Crescent Island	10.0 $\pm$ 0.0	30.0 $\pm$ 0.0	100.0 $\pm$ 0.0
Sher Karuturi	10.1 $\pm$ 0.1	32.3 $\pm$ 2.9	108.6 $\pm$ 17.3
Oserian	10.0 $\pm$ 0.0	30.0 $\pm$ 0.0	108.6 $\pm$ 17.3
Recommended Limit in $\mu\text{g/l}$			
HDL ^a	10.0	50.0	50.0
MPL ^a	10.0	1000.0	100.0
TC ^a	10.0	2 $\times$ 10 ³	100.0

HDL WHO highest desirable level in drinking water, *MPL* WHO maximum permissible level in drinking water, *TC* WHO threshold concentration for aquatic life tolerance (safe for most fish)

^a WHO Drinking water standards (1993)

T-test results (Table 13) showed that there is no significant difference ($p = 0.326$) in the means of Cd concentration and the recommended limits (HDL, MPL and TC) and Pb concentration ($P = 0.009$) with the recommended limits (MPL and TC). However, the difference in the means of Cu (HDL, MPL and TC) and Pb (HDL) concentration with the respective recommended limits is statistically significant at 5% significance level ($p = 0.000$).

Table 15: T-test for Cd, Cu and Pb in water with the recommended limits

	Mean difference	t	df	P-value
Cd concentration (mg/kg) - HDL	0.008	1.000	27	0.326
Cd concentration (mg/kg) - MPL	0.008	1.000	27	0.326
Cd concentration (mg/kg) - TC	0.008	1.000	27	0.326
Cu concentration (mg/kg) - HDL	-19.667	-80.934	27	0.000
Cu concentration (mg/kg) - MPL	-969.667	-3990.253	27	0.000
Cu concentration (mg/kg) - TC	-1.997E4	-82176.637	27	0.000
Pb Concentration (mg/kg) - HDL	67.794	10.651	27	0.000
Pb Concentration (mg/kg) - MPL	17.794	2.796	27	0.009
Pb Concentration (mg/kg) - TC	17.794	2.796	27	0.009

Most of the heavy metal concentrations were recorded at the detection limits (Pb – 100 ppb, Cu – 30 ppb and Cd – 10 ppb) of the AAS; taking cadmium for instance, all the stations recorded a mean concentration of 10.0 µg/L which was within the 10 µg/L WHO Highest Desirable Level (HDL) of drinking water except Sher Karuturi which recorded 10.1 µg/L. Mean copper concentrations were below the 50.0 µg/L WHO Highest Desirable Level (HDL) of drinking water. Mean lead concentrations in all the stations were elevated above the 50 µg/L WHO Highest Desirable Level (HDL) of drinking water (Table 13). The data therefore indicates that the water concentrations of Cu and Cd in Lake Naivasha waters were within normal range with exceptions of elevated lead concentrations. Comparing the data with Ochieng *et al.*, (2007) Cd, Cu and Pb concentrations were recorded at 8.0 µg/L, 4.7 µg/L and 42.1 µg/L respectively which were all below the recommended WHO (1993) drinking water limits. The variation in metal concentrations could be explained by the fact that metals get enriched by aquatic organisms which convert them into complexes which may be even more toxic in aquatic environments (Jain, 2004). The distribution processes of the metals entering natural waters are controlled by a dynamic set of physical–chemical interactions and equilibria and their solubilities are principally controlled by pH, concentration, type of metal species, organic ligands, the

oxidation state of mineral components and the redox environment of the aquatic system (Warren *et al.*, 2005; Grosbois *et al.*, 2006).

Lake Naivasha is an important source of drinking and irrigation water for many inhabitants surrounding the aquatic ecosystem. Anthropogenic and geological disturbances, such as contaminated surface water inflows and soil erosion, siltation, and industrial effluents are expected to influence the organic and inorganic loads which would register significant footprints in water.

Other similar studies in the Rift valley lakes of Kenya indicate that Cd, Cu and Pb concentrations were at 5 µg/L, 15 µg/L and 65 µg/L in Lake Elementaita. Cadmium and copper were within the recommended limits, however lead was above the 50 µg/L WHO HDL Limit. Similarly, Lake Nakuru reportedly had mean Cd, Cu and Pb concentrations at 3.0 µg/L, 5.0 µg/L and 106.0 µg/L in compliance with WHO limits with an exception of lead (Ochieng *et al.*, 2007). It is clear that discharged waters with anthropogenic influence in Lake Naivasha maintain the highest lead concentrations. The highest possibility is that lead can be found as an ingredient in many industrial activities surrounding the Lake; for instance as an impurity in fertilizers, in composts and manure, in sewage sludge, in batteries among others. Lead could also be abundant in the waters in dissolved form due to the fact that it is not an essential trace element for biological systems and thus remains either in solution or as depositions in sediment. pH also contributes to the increased concentrations of lead as at pH greater than 8.5, its toxicity increases in contrary to Cd and Cu. Mouth of Malewa, Mouth of Karati and Oserian discharge outlets exhibited high lead concentrations with pH levels greater than 8.5 that contribute to its enhanced bioavailability and thereby toxicity. The sites exhibiting high leads contents clearly indicate that lead concentration in water could be influenced by river inflow and runoff from various Lakeside cultivation activities (Hubble and Harper, 2001).

4.4 Heavy metal concentrations in *C. carpio* muscle tissues

C. carpio was assayed for heavy metal concentrations (detection limits; Pb 0.1 ppm, Cd 0.01 ppm and Cu 0.03 ppm) and the results are presented in Table 14 below.

4.4.1 Cadmium concentrations in *C. carpio* muscle tissues

The mean cadmium concentrations in *C. carpio* muscle tissue ranged from 1.1 mg/kg to 1.7 mg/kg (Table 14). Muscle tissues of *C. carpio* from Kasarani recorded high lead concentrations 1.7 mg/kg whilst muscle tissues of *C. carpio* from Mouth of Malewa and Sher Karuturi were the lowest 1.1 mg/kg. The two major large scale flower farms Sher Karuturi and Oserian discharge outlets had remarkably lower mean cadmium concentration in the *C. carpio* muscle tissues (1.1 mg/kg and 1.3 mg/kg) than those found at the Kasarani small scale flower farm discharge outlets which recorded 1.7 mg/kg. *C. carpio* muscle tissues from Hippo point and Kasarani had similar mean cadmium concentration of 1.6 mg/kg.

Table 16: Cadmium concentration (mg/kg) in *C. carpio* muscle tissues between March and May 2010

Sampling stations	Mean concentration $\pm$ STDEV
Hippo point	1.6 $\pm$ 0.2
Kasarani	1.7 $\pm$ 0.8
Mouth of Malewa	1.1 $\pm$ 0.0
Mouth of Karati	1.1 $\pm$ 0.0
Crescent Island	1.6 $\pm$ 0.6
Sher Karuturi	1.1 $\pm$ 0.1
Oserian	1.3 $\pm$ 0.1

STDEV Standard Deviation

One way ANOVA revealed that the difference in the means of Cd concentrations in *C. carpio* muscle tissues for the sampling stations is not statistically significant at 5% significance level ($p = 0.166$, Appendix III). LSD was therefore not performed.

4.4.2 Copper concentrations in *C. carpio* muscle tissues

The highest mean copper concentration was recorded in two stations; Mouth of Malewa 2.2 mg/kg and Sher Karuturi 2.2 mg/kg (range 1.5 – 2.2 mg/kg). Low mean copper

concentrations 1.5 mg/kg occurred at Kasarani, Mouth of Karati and Crescent Island sampling stations. Table 15 below shows the Copper concentrations in *C. carpio* muscle tissues in Lake Naivasha.

Table 17: Copper concentration (mg/kg) in *C. carpio* muscle tissues between March and May 2010

Sampling station	Mean concentration $\pm$ STDEV
Hippo point	1.6 $\pm$ 0.2
Kasarani	1.5 $\pm$ 0.0
Mouth of Malewa	2.2 $\pm$ 0.3
Mouth of Karati	1.5 $\pm$ 0.0
Crescent Island	1.5 $\pm$ 0.0
Sher Karuturi	2.2 $\pm$ 0.3
Oserian	1.8 $\pm$ 0.3

STDEV Standard Deviation

One way ANOVA (Appendix III) and LSD results showed a statistically significant difference ($p= 0.000$ at 5% significance level) in the mean Copper concentration of *C. carpio* muscle tissues in the seven sampling sites at the pairs of stations presented in Table 16 below.

Table 18: LSD for Copper concentration in *C. carpio* muscle tissues among the different sample stations in Lake Naivasha.

(I) Sampling stations	(J) Sampling stations	Mean Difference	
		(I-J)	Sig.
Hippo point	Sher Karuturi	-0.6*	0.000
Kasarani	Mouth of Malewa	-0.6*	0.000
Kasarani	Sher Karuturi	-0.8*	0.000
Kasarani	Oserian	-0.3*	0.039
Mouth of Malewa	Hippo point	0.5	0.006
Mouth of Malewa	Kasarani	0.6*	0.000
Mouth of Malewa	Mouth of Karati	0.6*	0.000
Mouth of Malewa	Crescent Island	0.6*	0.000
Mouth of Karati	Mouth of Malewa	-0.6*	0.000
Mouth of Karati	Sher Karuturi	-0.8*	0.000
Mouth of Karati	Oserian	-0.3*	0.039
Crescent Island	Sher Karuturi	-0.8*	0.000
Crescent Island	Oserian	-0.3*	0.039
Sher Karuturi	Oserian	0.5	0.006

* Significant ($P < 0.05$)

4.4.3 Lead concentrations in *C. carpio* muscle tissues

The mean Lead concentration in *C. carpio* muscle tissues was invariably high ranging from 5.2 mg/kg – 58.1 mg/kg. High concentration 58.1 mg/kg occurred for *C. carpio* muscle tissues from Mouth of Malewa and low concentration for *C. carpio* muscle tissues (5.2 mg/kg) from Crescent Island (Table 17). There was a statistically significant difference ($p = 0.000$) in mean lead concentrations in *C. carpio* in the seven sampling sites at 5 % significance level (One way ANOVA, Appendix III). LSD results presented in Table 18 indicated significant mean differences in sampling sites.

Table 19: Lead concentration (mg/kg) in *C. carpio* muscle tissues between March and May 2010

Sampling Station	Mean concentration $\pm$ STDEV
Hippo point	33.6 ± 3.6
Kasarani	15.1 ± 6.7
Mouth of Malewa	58.1 ± 2.8
Mouth of Karati	48.0 ± 2.3
Crescent Island	5.2 ± 0.4
Sher Karuturi	41.2 ± 2.4
Oserian	29.5 ± 6.4

STDEV Standard Deviation

All the sampling stations have a significantly different level ($p = 0.000$) of mean lead concentration in *C. carpio* muscle tissues.

Table 20: LSD for Lead concentration in *C. carpio* muscle tissues among the different sample stations in Lake Naivasha.

(I) Sampling stations	(J) Sampling stations	Mean Difference (I-J)	Sig.
Hippo point	Kasarani	18.5*	0.000
Hippo point	Mouth of Malewa	-24.5*	0.000
Hippo point	Mouth of Karati	-14.4*	0.000
Hippo point	Crescent Island	28.4*	0.000
Hippo point	Sher Karuturi	-7.6*	0.017
Kasarani	Mouth of Malewa	-43.0*	0.000
Kasarani	Mouth of Karati	-32.9*	0.000
Kasarani	Crescent Island	9.8*	0.003
Kasarani	Sher Karuturi	-26.2*	0.000
Kasarani	Oserian	-14.4*	0.000
Mouth of Malewa	Mouth of Karati	10.1*	0.002
Mouth of Malewa	Crescent Island	52.9*	0.000
Mouth of Malewa	Sher Karuturi	16.8*	0.000
Mouth of Malewa	Oserian	28.6*	0.000
Crescent Island	Sher Karuturi	-36.0*	0.000
Crescent Island	Oserian	-24.2*	0.000
Sher Karuturi	Hippo	7.6*	0.017
Sher Karuturi	Oserian	11.8*	0.001

* Significant ($P < 0.05$)

4.4.4 Cd, Cu and Pb concentrations in *C. carpio* muscle tissues and comparison with recommended limits

The data indicates that lead is the most predominant metal in *C. carpio* followed by cadmium and copper respectively. The highest lead content is found in *C. carpio* caught at the Mouth of Malewa with the lowest concentration in *C. carpio* caught at Crescent Island. Comparing the data with the tolerable values of heavy metals in fish; the mean concentrations of cadmium and lead were found to exceed the recommended tolerable values while those of copper were low (Table 19).

Table 21: Cadmium, Copper and Lead concentration in the Lake Naivasha *C. carpio* muscle tissues and comparison with the tolerable values

Sampling Station	Mean concentration $\pm$ Standard deviation		
	Cadmium (mg/kg)	Copper (mg/kg)	Lead (mg/kg)
Hippo point	1.6 $\pm$ 0.2	1.6 $\pm$ 0.2	33.6 $\pm$ 3.6
Kasarani	1.7 $\pm$ 0.8	1.5 $\pm$ 0.0	15.1 $\pm$ 6.7
Mouth of Malewa	1.1 $\pm$ 0.0	2.2 $\pm$ 0.3	58.1 $\pm$ 2.8
Mouth of Karati	1.1 $\pm$ 0.0	1.5 $\pm$ 0.0	48.0 $\pm$ 2.3
Crescent Island	1.6 $\pm$ 0.6	1.5 $\pm$ 0.0	5.2 $\pm$ 0.4
Sher Karuturi	1.1 $\pm$ 0.1	2.2 $\pm$ 0.3	41.2 $\pm$ 2.4
Oserian	1.3 $\pm$ 0.1	1.8 $\pm$ 0.3	29.5 $\pm$ 6.4
Reference Limit			
UNEP 1985 ^a	0.3	NL	0.3
IAEA - 407 ^b	0.18	3.28	0.12
Directive 2005/78/EC ^a	0.05	NL	0.02

^a Ozturk *et al.*, (2009), ^b Wyse *et al.*, (2003)

NL Not in Literature

T-test results showed a significant difference ($p = 0.000$) in the means of the recommended limits and the observed concentration of Cd, Cu and Pb in the *C. carpio* muscle tissues in all the cases (Table 20).

Table 22: T-test for Cd, Cu and Pb in *C. carpio* muscle tissues with the recommended limits

	Mean difference	t	P-value
Cd concentration (mg/kg) - UNEP	1.05	11.946	0.000
Cd concentration (mg/kg) - IAEA_407	1.17	13.312	0.000
Cd concentration (mg/kg) - EC	1.30	14.793	0.000
Cu Concentration (mg/kg) - IAEA	-1.51	-22.241	0.000
Pb Concentration (mg/kg) - UNEP	32.67	9.750	0.000
Pb Concentration (mg/kg) - IAEA_407	32.84	9.804	0.000
Pb Concentration (mg/kg) - EC	32.94	9.833	0.000

Among the key factors significant for the accumulation of metals by fish include fish location, feeding behavior, trophic level and physical - chemical properties of water (Kargin 1996; Sankar *et al.*, 2006). Ideally *C. carpio* confine themselves to restricted discrete localities (sites) and do not transcend long distances (Crook, 2009; Jones and Stuart, 2009; Khan *et al.*, 2003; Koehn, 2004) being benthic foragers. They instead spend most of their time churning at the bottom, an element that does not give them a chance to move widely. A capture – recapture study undertaken in Lake Naivasha to understand *C. carpio* movement revealed a home range of about 50 m (Oyugi, 2010). The data obtained in this study therefore signifies Cadmium, Copper and Lead concentration in *C. carpio* within their localized home ranges. Baseline data and knowledge of heavy metal concentration in aquatic ecosystems is thus vital in management for various purposes such as the risk of taking contaminated fish as part of human diet and metal pollution control strategies. Most fish are on top of the trophic chain and have the potential to accumulate high metal content even in mild polluted waters, thus metals concentration in fish could be used as an index to estimate the level of pollution in lake waters.

Fish, particularly introduced benthivorous species like *C. carpio* and organisms up its trophic chain are more likely to be impacted adversely by the heavy metals as it forms a major component (89 %; Naivasha fisheries station annual report, 2008) of the Lake Naivasha fishery consumed by majority of the population in Naivasha. The consequence to the consumers would be of chronic impact; as heavy metals tend to increase in concentration in a biological organism over time, compared to the chemical's concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.

Fish is a good bio-indicator because of the ease to obtain it in large quantities (easy sampling), potential to accumulate heavy metals, long life span and optimum size for analysis (Batvari *et al.*, 2007). In Avsar dam, Turkey; Ozturk *et al.*, (2009), obtained Cd 0.17 mg/kg, Cu 3.85 mg/kg and Pb 2.14 mg/kg in *C. carpio* muscle tissues. In comparing the data with the findings of this study, Avsar dam had elevated copper concentrations in *C. carpio* muscle tissues. On contrary Lake Naivasha has high Pb concentration in *C. carpio* muscle tissues. The differences could be due to different sources. The high cadmium and lead levels in *C. carpio* from Lake Naivasha are anthropogenic and more so derived from benthivorous material in sediments especially at shallow areas in Lake Naivasha, an indication that pollution in Lake Naivasha is beyond the tolerable values for human health in fish (Table 19). Cadmium for example is a typical example of a cumulative poison whose prolonged uptake interferes with the function of the kidneys and liver in aquatic and human health (Rishi and Jain, 1998). Bone tissue is affected too as cadmium disturbs the metabolism of calcium (Smirjchkova *et al.*, 2005). Lead on the other hand interferes with the hormonal profiles of fish involved in the maintenance of ionic and osmotic balance, energy metabolism and reproduction consequently leading to the inactivation of enzymes and proteins (Ramesh *et al.*, 2009). In human health, fish consumption is strongly correlated with cadmium and lead accumulation, as the metals are known nephrotoxics that induce oxidative stress and damage to the proximal renal tubule, the location where nearly all renal cell cancers arise (Wilson *et al.*, 2009). Lead in particular has been documented to result in human disorders of the nervous system, peripheral nervous system, growth and development, cognitive development, behavior, hearing, sight, muscular movement, digestive system, kidney and blood in children (Silbergeld, 1997). In foetus, lead will result in

reduced birth weight and kidney, nervous, cardiovascular and circulation disorders in adults (National Research Council (US), 1993).

The abundance of lead and cadmium could be due to the fact that they are non-essential heavy metals in organisms and thus are deposited in tissues while low copper concentration could be due to the fact that copper is an essential enzymatic element utilized in fish metabolism. Crescent Island (control station) recorded low concentrations of lead and cadmium (Table 19) in *C. carpio* muscle tissues. The reason could be due to less influx of human influenced activities around and in the Lake which could render contamination of the sediments, water and *C. carpio*. Low copper concentration could be as a result of reduced bioavailability especially noting that its levels are quite low in water and sediments as well. In addition copper is an essential element for biological systems and thus its uptake by organisms in Lake Naivasha could be another factor contributing to its low concentration. Mouth of Malewa, Mouth of Karati and Sher Karuturi had high levels of lead concentration in *C. carpio* as they are key areas of contaminant entry into lake through contaminated inflows and effluent discharge. Of interest to note is that *C. carpio* population is the highest at these sites and that they form its principal feeding and breeding grounds due to the shallow turbid waters with vegetative sediments. *C. carpio* mean lead concentration at Kasarani is low, possibly due to the nature of small scale activities around the site whose effect may not be significant. In terms of lead and cadmium concentration, *C. carpio* muscle tissues from Hippo point (control site) had peculiarly high concentrations above the required limit. One clear reason would be due to influence from the Oserian and Kasarani stations which are in close proximity and are characterized by effluent discharge in addition to natural metal concentrations that *C. carpio* would have absorbed from sediments. In general, cadmium, Copper and lead concentrations of *C. carpio* at Kasarani, Mouth of Malewa, Mouth of Karati, Sher Karuturi and Oserian are influenced by site activities most of which are characterized by agricultural effluent discharge (Sher Karuturi, Oserian and Kasarani) and surface inflows (contaminated) from the catchment (Mouth of Malewa and Mouth of Karati). Elevated cadmium levels from *C. carpio* could be due to the fact that it is a non-essential metal and less bio-utilization in the tissues which renders its accumulation.

4.5 Variation of heavy metal concentrations in lake sediments, water and in *C. carpio* muscle tissues

The variation of cadmium, copper and lead concentration in lake sediments, water and *C. carpio* muscle tissues was analyzed via a two way ANOVA. The metals concentration was analyzed with regards to the matrix and the sampling site. Specific analyses are presented in the following subsections.

4.5.1 Cadmium concentration in lake sediments, water and in *C. carpio* muscle tissues

To establish the variation of mean cadmium concentration in sediments, water and *C. carpio* muscle tissues, a comparison in concentration was done among the three matrices in the seven sampling sites. Data indicated that sediments contain high cadmium concentration and especially from Oserian flower farm discharge outlet 5.4 mg/kg (ppm) followed by *C. carpio* muscle tissues at Kasarani 1.7 mg/kg and water at Sher Karuturi 10.1 µg/l (0.01 ppm) (Figure 6). This therefore follows that mean cadmium concentration in the three matrices in increasing order follows the variation water < *C. carpio* muscle tissues < sediment in all the seven sampling stations.

Two way ANOVA for cadmium concentrations in lake sediments, water and in *C. carpio* muscle tissues was performed (Appendix IV). Results revealed a significant difference ($p = 0.000$) in the mean concentration of Cadmium as per the sampling sites, the matrices (lake sediments, water and in *C. carpio* muscle tissues) and the interaction between the matrix and the sampling sites at 5% significance level. The variations in the differences in the means of cadmium concentration in various sampling sites as per the given matrices are presented in Figure 6.

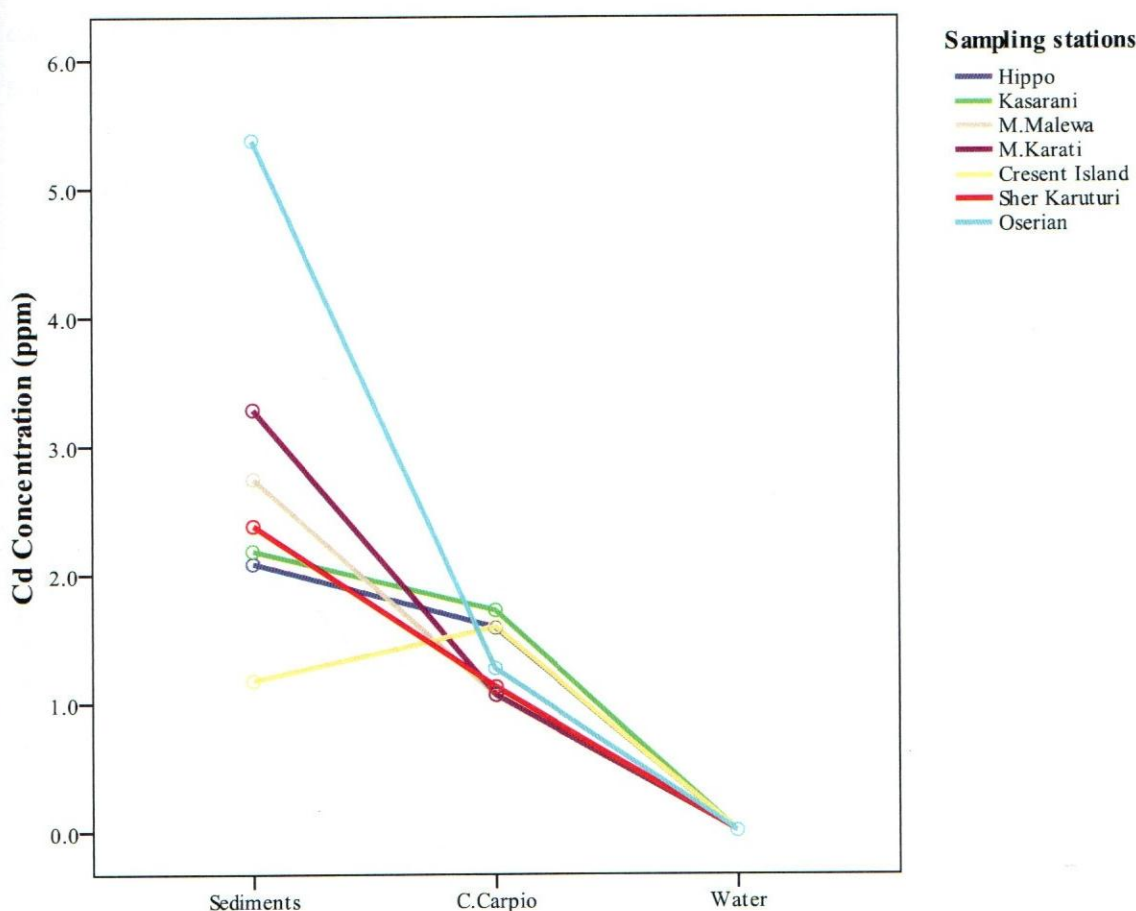


Figure 6: Mean cadmium concentration variation in sediments, *C. carpio* and water

4.5.2 Copper concentrations in lake sediments, water and in *C. carpio* muscle tissues

The variation of mean copper concentration in Lake Sediments, water and *C. carpio* muscle tissues are presented in Figure 7. Sediments from Mouth of Malewa contain the highest copper concentration 8.4 mg/kg (ppm), followed by *C. carpio* muscle tissues from mouth of Malewa and Sher Karuturi 2.2 mg/kg with water being the lowest at 30.0 (0.03 ppm) $\mu\text{g/l}$ in all the sampling stations except Sher Karuturi which recorded 32.3 (0.032 ppm) $\mu\text{g/L}$. The variation of mean copper concentration in lake sediments, water and *C. carpio* muscle tissues follows water < *C. carpio* muscle tissues < Sediments in increasing order in all the seven sampling stations (Figure 7).

Two way ANOVA for copper concentrations in lake sediments, water and in *C. carpio* muscle tissues (Appendix IV) revealed a significant difference ($p = 0.000$) in the mean concentration of copper as per the sampling sites, the matrices (lake sediments, water and in *C.*

carpio muscle tissues) and the interaction between the matrix and the sampling sites at 5% significance level.

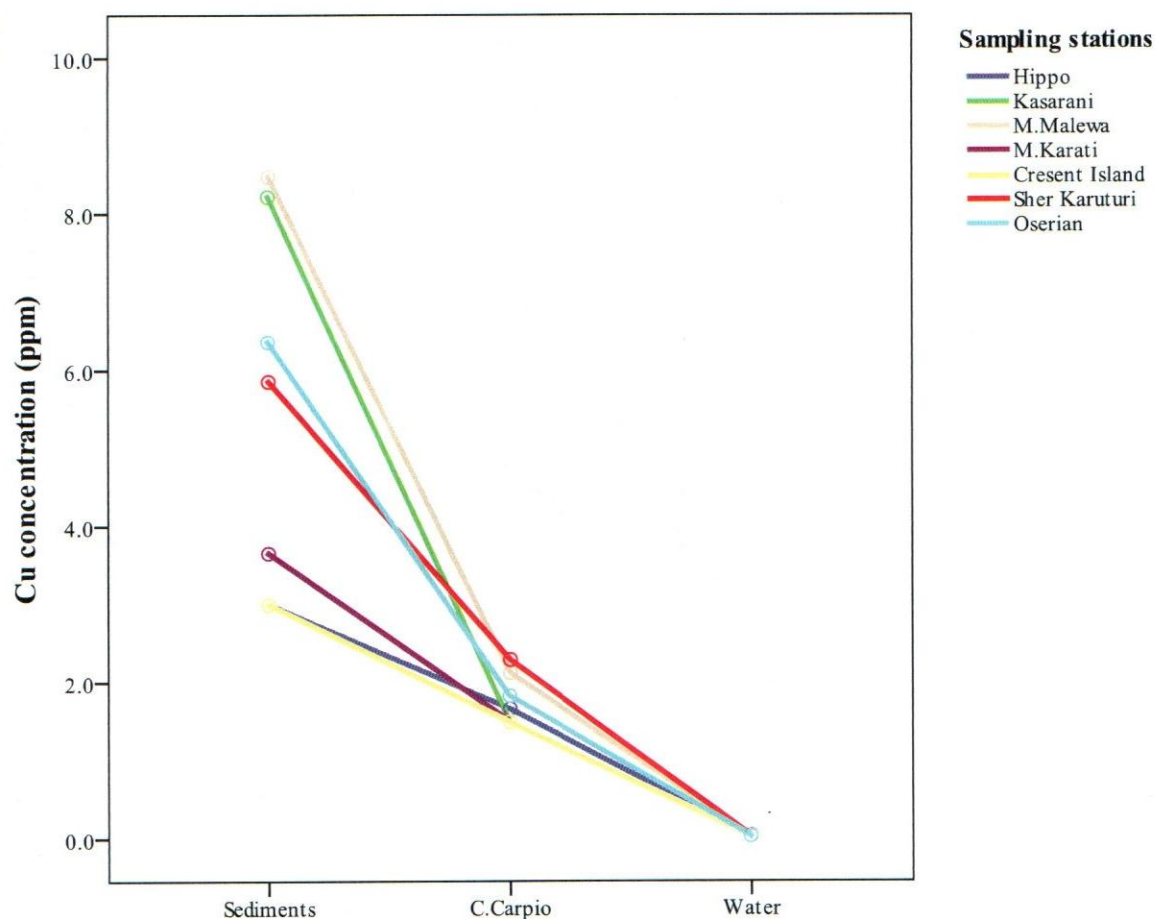


Figure 7: Mean copper concentration variation in sediments, *C. carpio* and water

4.5.3 Lead concentrations in lake sediments, water and in *C. carpio* muscle tissues

The mean lead concentration is highest in sediments from Mouth of Malewa 53.1 mg/kg, followed by *C. carpio* muscle tissues from Mouth of Malewa 58.1 mg/kg and water from Mouth of Malewa 179.8 (0.179 ppm) $\mu\text{g/L}$. Mean lead concentration in the seven sampling sites in the three matrices follow the variation; water < *C. carpio* muscle tissues < sediments in increasing order in the seven sampling sites (Figure 8).

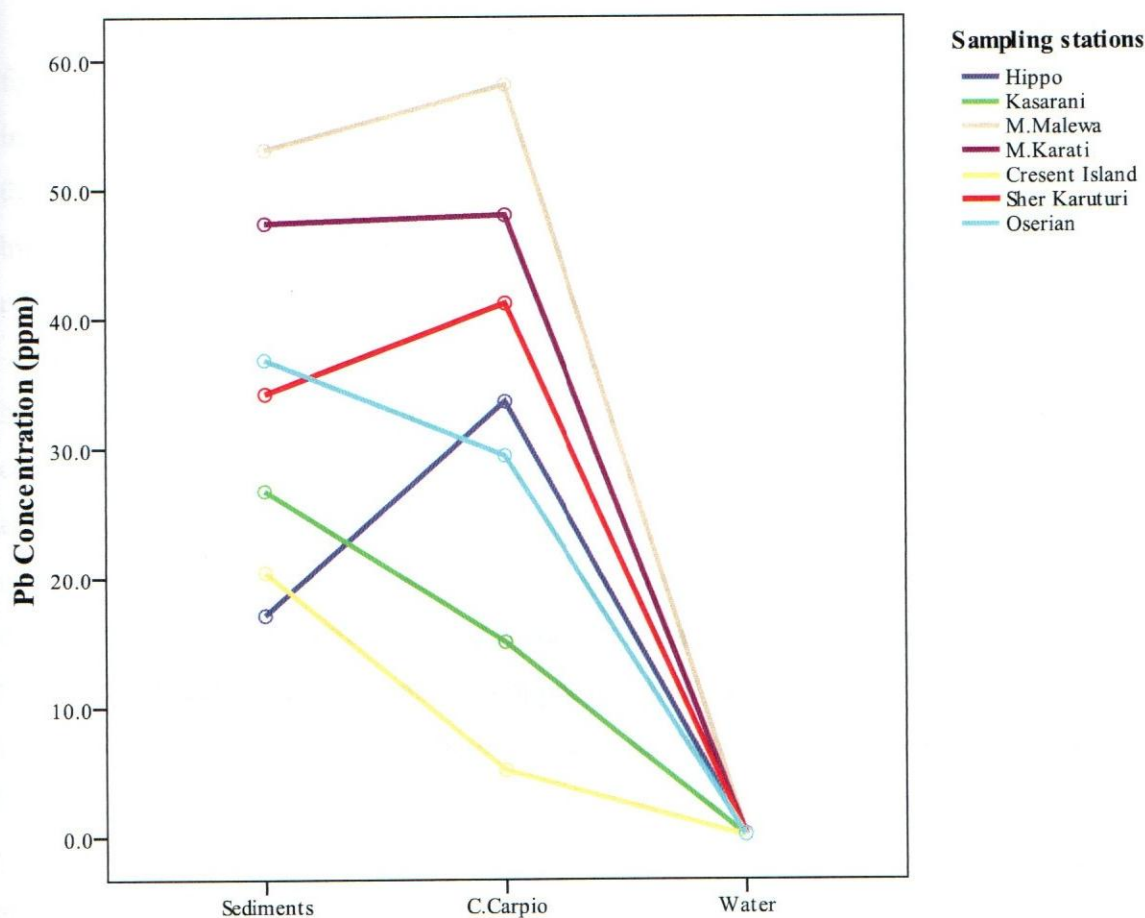


Figure 8: Mean lead concentration variation in sediments, *C. carpio* and water

Two way ANOVA indicates a significant difference in the mean concentration of lead as per the sampling sites, the matrices (lake sediments, water and in *C. carpio* muscle tissues) and the interaction between the matrix and the sampling sites at 5% significance level ($p = 0.00$) (Appendix IV).

The mean concentration of cadmium, copper and lead in Lake Naivasha follows the variation water < *C. carpio* muscle tissues < sediment in increasing order. With respect to anthropogenic influence, sediments play a major role in transportation, deposition and adsorption of heavy metals into aquatic environments. Thus, concentrations of heavy metals in sediment play an important role in providing information about overlying water quality (Jaysankar *et al.*, 2009).

According to Ahmad and Shuhaimi-Othman (2010), in an aquatic system, pollutants will form as deposits in sediments which naturally consist of a complex mixture of organic and inorganic components like clays, silicates, carbonate, sulphide, minerals and bacteria. They are therefore well known sinks for metal contaminants. Physical-chemical absorption from water, biological intake and accumulation of metals that are enriched with particles form the major mechanisms of heavy metals intake by sediments.

Data obtained indicates that the abundance of cadmium, copper and lead in Lake Naivasha is contained in sediments followed by *C. carpio* muscle tissues with very little concentrations in water. Underscoring the fact that all stations analysed were considered polluted and unpolluted, sediments still yielded high heavy metal concentrations in all sites. Sediments can therefore archive ecological information; as each time precipitation, runoff, erosion and deposition occurs, the concentrations of heavy metals tend to increase. This marks the reason why sediments have more cadmium, copper and lead concentrations in the stations considered polluted and low metals concentration in the unpolluted stations. In addition, Lake Naivasha being a volcanic Lake there exist natural background concentrations of heavy metals in its geology which are as well deposited and accumulate as heavy metals in the sediments. The Lake and its catchment are dynamic in nature with various anthropogenic and ecological processes taking place, hence experiences a lot of heavy metal speciation, with several distinct geochemical phases, such as clay minerals, organic matter, carbonates and sulphates. The types of reactions that are likely to control the partitioning of metals in sediment are: adsorption and desorption, precipitation and solubilization, surface complex formation, ion exchange and biological mobilization or immobilization which often sink and accumulate in sediments (Alloway *et al.*, 1993). Sediments are therefore the ultimate recipients of cadmium, copper and lead in Lake Naivasha and overtime with runoff and deposition from the Mouths of River Malewa and River Karati and effluent discharge from the large (Oserian and Sher Karuturi) and small scale flower farms (concentrated around Kasarani), their concentration increases.

Fish on the other hand and in particular benthivorous species like the *C. carpio* who suck in prey items with sediments pose a high risk of heavy metal accumulation in their biological systems especially the non-essential heavy metals like cadmium and lead. However, even when the essential elements like copper exceed the required limits they become toxic and adsorb in fish tissues. Overtime as the *C. carpio* feeds, ages and reproduces; putting into context the

concept of bio-accumulation from sediments, the concentration of heavy metal increases more than it was before, rendering its bioavailability toxic. However this concentration is chronic and is prolonged for it to achieve a higher concentration as compared to sediments. It is quite evident that *C. carpio* will have less concentration than sediments as it picks its food items from sediments which contain numerous amounts of cadmium, copper and lead concentrations.

Water quality on the other hand is dependent on several factors and especially heavy metal concentration in sediments. The chemical composition of inland aquatic ecosystems influences to a great extent the speciation of heavy metals. In the sampled (in this study) waters, (which mostly is turbid) a large proportion of heavy metals are bound to organic and inorganic particulate matter. Other factors which influence speciation are: pH, and dissolved organic matter. Large amounts of dissolved organic complexes and particulate matter with heavy metals are transported great distances to end up in the sediments. Water in this case acts as a recipient and carrier of cadmium, copper and lead and will ultimately deposit dissolved organic and inorganic complexes into sediments, which are later taken in by *C. carpio* as food.

Generally sediments hold greater than 99% of total quantity of a metal present in an aquatic system (Netpae & Phalaraksh, 2009). The variation illustrated in this study for Lake Naivasha indicates 1 - 288 times greater cadmium, copper and lead concentration in sediment than in *C. carpio* muscle tissues and water. In addition, the concentration of cadmium, copper and lead was 59 – 281 times more in *C. carpio* muscle tissues than in water (Table 23).

Table 23: Magnitude of Cd, Cu and Pb concentration in sediments over *C. carpio* muscle tissues and water and *C. carpio* muscle tissues over water in Lake Naivasha

Metal/Matrix	Mean concentration (ppm) $\pm$ STDEV			Magnitude		
	Sediment	<i>C. carpio</i>	Water	Sediment/ <i>C. carpio</i>	Sediment/water	<i>C. carpio</i> /water
Cadmium	2.75 $\pm$ 1.4	1.35 $\pm$ 0.4	0.01 $\pm$ 0.04	2	275	135
Copper	5.51 $\pm$ 2.3	1.76 $\pm$ 0.3	0.03 $\pm$ 1.2	3	184	59
Lead	33.7 $\pm$ 12.9	32.9 $\pm$ 17.7	0.117 $\pm$ 33.6	1	288	281

Similarly, Öztürk *et al.*, (2009); Demark *et al.*, (2006) and Klavins *et al.*, (2000) obtained high metal content in sediment than in water and fish. The heavy metal concentrations were 100-10,000 times greater in the sediment than the water in Yangtze river (Yi *et al.*, 2008) and in Avsar dam Lake, 214 – 385 higher in *C. carpio* muscle tissues than in water (Öztürk *et al.*, 2009).

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary

The findings of this study indicate the presence of heavy metal concentration in sediment, water and *C. carpio* muscle tissues from Lake Naivasha. The range of physical – chemical water quality parameters (pH, temperature, transparency, Conductivity, TDS and DO) from all the seven sampling stations indicate that the Lake Naivasha waters are within the required relevant regulatory requirements (WHO and Water quality regulations of Kenya).

5.2 Conclusions

Based on the study objectives, research questions and data analysis of this study, the following major research findings are established:

- a) The mean concentration of Cd, Cu and Pb in sediments from Lake Naivasha was 2.75 mg/kg (± 1.4), 5.51 mg/kg (± 2.3) and 33.7 mg/kg (± 12.9) respectively.
- b) In water from Lake Naivasha, mean of Cd, Cu and Pb concentration were 0.01 mg/l (± 0.04), 0.03 mg/l (± 1.2) and 0.117 mg/l (± 33.6) respectively.
- c) The mean concentration of Cd, Cu and Pb in *C. carpio* muscle tissues from Lake Naivasha was 1.35 mg/kg (± 0.4), 1.76 mg/kg (± 0.3) and 32.9 mg/kg (± 17.7) respectively.
- d) Using the NOAA (2009) Threshold Effect Concentration (TEC) Sediment Quality Guidelines of cadmium 0.99 mg/kg, copper 31.6 mg/kg and lead 35.8 mg/kg; only cadmium 2.75 mg/kg (± 1.4) in sediments from Lake Naivasha exceeded the recommended TEC limit. In Lake Naivasha waters, the concentration of cadmium and copper was within the normal range of WHO (1993, 2008) requirements with exceptions of elevated lead concentration at 117 $\mu\text{g/l}$ above the WHO 50 $\mu\text{g/l}$ HDL in drinking water. In *C. carpio* muscle tissues, the mean concentration of cadmium 1.35 ppm (± 0.4) and lead 32.9 ppm (± 17.7) was found to exceed the recommended UNEP; 1985 (Cd, Pb – 0.3 ppm, 0.3 ppm), IAEA - 407 (Cd, Pb – 0.18 ppm, 0.12 ppm) and Directive 2005/78/EC (Cd, Pb – 0.05 ppm, 0.02 ppm) tolerable values while those of copper recorded lower than the guidelines.

- e) Comparing the concentrations of cadmium, copper and lead in sediment, water and *C. carpio* muscle tissues in Lake Naivasha, the variation shows high accumulated metals in sediments followed by fish and water.
- f) Following the elevated heavy metal concentration in *C. carpio* muscle tissues; consumption of the same by human beings and other higher trophic organisms is alarming as the consequences could be chronic and severe in the long term due to the risk of bio-accumulation and bio-magnification.

5.3 Recommendations

In view of the above conclusions, this study puts forth the following recommendations:

- a) Documentation and subsequent regulation of the types and amounts of agrochemicals in use around the lake and its catchment containing lead and cadmium as they occurred as the most prominent metals in sediments, water and *C. carpio* muscle tissues especially near the flower farm wetland discharge outlets and river mouths.
- b) Restriction and reduction by the local authorities of further increase in horticultural and settlement activities around the shore; in addition to continuous monitoring of effluent discharged by existing human based activities in the lake to check and manage lead and cadmium levels to sustainably manage pollutant influx into the lake ecosystem .
- c) Conservation education and awareness through policy briefs to the flower farms and communities that live in the catchment, especially those along the banks of the Malewa and Karati on sustainable agricultural practices with respect to minimal use of agrochemicals that contain lead, cadmium and copper as active ingredients.
- d) Continuous assessment and monitoring of cadmium, copper and lead concentration in Lake Naivasha especially in sediments, water and *C. carpio* muscle tissues. Key attention should be focused on flower farm discharge outlets and surface water inflows to enable implementation of monitoring plans which can enhance conservation of ecological resources within the Ramsar site.

- e) An alternative delicacy to consumers of *C. carpio* in Lake Naivasha to minimize the possibility of heavy metal bio-magnification whose consequence includes amongst others kidney problems, lung cancer, bone and reproduction defects in human health.

5.3.1 Suggestions for further research

Further research in Lake Naivasha is suggested in the following:

- a) Sources of lead and cadmium in Lake Naivasha and their potential effect to water, sediment and *C. carpio* muscle tissues as they emerged the heavy metals with high concentration within the three matrices investigated.
- b) Seasonal cadmium, copper and lead determination in sediments, water and *C. carpio* to check and establish if seasonal changes have any influence in heavy metal concentration at the various matrices
- c) Determination of cadmium, copper and lead concentration in *C. carpio* intestines, liver, kidney, gills as these are significant areas of metabolic breakdown and assimilation in fish and could give vital information that could compare with the heavy metal concentration in muscle tissues. This is vital in terms of assessing the toxicity effects as ingested or absorbed metals could be partitioned and accumulated in other areas within the fish biological system
- d) Comparison of cadmium, copper and lead concentration in *C. carpio* tissues *vis a vis* fish age to be able to establish the variation and quantities of trace metal accumulation. This will help to understand if an increase in metal concentration in fish is dependent on age and to establish if the accumulated metals have a threshold upon which fish die on exposure.
- e) Determination of cadmium, copper and lead concentration in the *Eichhornia crassipes* (water hyacinth) of Lake Naivasha to further understand the dynamics of heavy metal concentration in the lake.
- f) Determination of the average daily intake of cadmium, copper and lead that consumers of *C. carpio* in Lake Naivasha are exposed to and associated health effects.

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APPENDIX I: ANOVA FOR HEAVY METAL CONCENTRATION IN SEDIMENTS

ANOVA for Cadmium Concentration in sediments in Lake Naivasha, Kenya

Matrix	Source of variation	Sum of Squares	Df	Mean Square	F	Sig.
Sediment	Between Groups	42.2	6	7.0	8.9	0.000
	Within Groups	16.6	21	0.8		
	Total	58.8	27			

ANOVA for Copper concentrations in sediments in Lake Naivasha, Kenya

	Source of variation	Sum of Squares	df	Mean Square	F	Sig.
Sediments	Between Groups	132.2	6	22.0	37.8	0.000
	Within Groups	12.2	21	0.5		
	Total	144.4	27			

ANOVA for Lead concentrations for Sediments in Lake Naivasha, Kenya

Matrix	Source of Variation	Sum of Squares	df	Mean Square	F	Sig.
Sediments	Between Groups	4283.5	6	713.9	64.2	0.000
	Within Groups	233.6	21	11.1		
	Total	4517.2	27			

APPENDIX II: ANOVA FOR HEAVY METAL CONCENTRATION IN WATER

ANOVA for Cadmium concentration on water

Matrix	Source of Variation	Sum of Squares	df	Mean Square	F	Sig.
Water	Between Groups	0.013	6	0.002	1.000	0.451
	Within Groups	0.046	21	0.002		
	Total	0.059	27			

ANOVA for Copper concentrations in water among the different sample stations in Lake Naivasha, Kenya

Matrix	Source of variation	Sum of Squares	df	Mean Square	F	Sig.
Water	Between Groups	18.559	6	3.093	2.490	0.056
	Within Groups	26.086	21	1.242		
	Total	44.644	27			

ANOVA for Lead Concentrations in water among the different sample stations in Lake Naivasha, Kenya

Matrix	Source of variation	Sum of Squares	df	Mean Square	F	Sig.
Water	Between Groups	20238.829	6	3373.138	6.817	.000
	Within Groups	10390.377	21	494.780		
	Total	30629.207	27			

APPENDIX III: ANOVA FOR HEAVY METAL CONCENTRATION IN *C. carpio* MUSCLE TISSUES

ANOVA for Cd concentration in *C. carpio* muscle tissues among the different sample stations in Lake Naivasha, Kenya

Matrix	Source of variation	Sum of Squares	Df	Mean Square	F	Sig.
<i>C. carpio</i>	Between Groups	1.919	6	0.320	1.718	0.166
	Within Groups	3.910	21	0.186		
	Total	5.829	27			

ANOVA for Copper concentration in *C. carpio* muscle tissues among the different sample stations in Lake Naivasha, Kenya

Matrix	Source of variation	Sum of Squares	df	Mean Square	F	Sig.
<i>C. carpio</i>	Between Groups	2.527	6	0.421	9.365	0.000
	Within Groups	0.944	21	0.045		
	Total	3.472	27			

ANOVA for Lead concentration in *C. carpio* muscle tissues among the different sample stations in Lake Naivasha, Kenya

Matrix	Source of variation	Sum of Squares	df	Mean Square	F	Sig.
<i>C. carpio</i>	Between Groups	8123.740	6	1353.957	78.944	.000
	Within Groups	360.168	21	17.151		
	Total	8483.908	27			

APPENDIX IV: ANOVA FOR VARIATION OF HEAVY METAL CONCENTRATIONS IN LAKE SEDIMENTS, WATER AND IN *C. carpio* MUSCLE TISSUES

ANOVA for cadmium concentrations in lake sediments, water and in *C. Carpio* muscle tissues

Source of variation	Sum of Squares	df	Mean Square	F	Sig.
Sampling site	11.941	6	1.990	6.100	0.000
matrix	104.995	2	52.498	160.896	0.000
Sampling site * matrix	32.144	12	2.679	8.210	0.000
Error	20.556	63	0.326		
Total	169.636	83			

ANOVA for Copper concentrations in lake sediments, water and in *C. Carpio* muscle tissues

Source of variation	Sum of Squares	df	Mean Square	F	Sig.
Sampling site	50.233	6	8.372	40.050	0.000
matrix	438.987	2	219.494	1050.003	0.000
Sampling site * matrix	84.506	12	7.042	33.688	0.000
Error	13.170	63	0.209		
Total	586.896	83			

ANOVA for Lead concentrations in lake sediments, water and in *C. Carpio* muscle tissues

Source of variation	Sum of Squares	df	Mean Square	F	Sig.
Sampling site	7258.997	6	1209.833	128.350	0.000
matrix	20591.449	2	10295.724	1092.27	0.000
Sampling site * matrix	5148.279	12	429.023	45.515	0.000
Error	593.840	63	9.426		
Total	33592.565	83			

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