INFLUENCE OF ANTHROPOGENIC ACTIVITIES ON SEDIMENT CHARACTERISTICS AND HEAVY METAL CONCENTRATIONS IN LAKE BARINGO, KENYA

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A Thesis submitted to the Graduate School in partial fulfilment for the requirements of the Degree in Master of Science in Environmental Science of Egerton University.

EGERTON UNIVERSITY

OCTOBER, 2015

DECLARATION AND RECOMMENDATION

DECLARATION

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

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RECOMMENDATION

This thesis has been submitted for examination with our approval as University Supervisors

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DEDICATION

To my parents, Richard and Anne Koskey; you are an inspiration to my everyday life.

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ABSTRACT

Lake Baringo waters and sediments are being impacted negatively by metal contaminants sourced from the lake's watershed posing a human and environmental health concern. The main objective was to determine the concentration of heavy metals cadmium (Cd), copper (Cu), mercury (Hg) and lead (Pb) in water and sediments, and to characterize sediments in terms of grain size and total organic carbon and relate them to the heavy metal levels encountered at the sampled sites. 5 sites were selected and samples collected over a period of six months. Water samples were collected in polypropylene bottles and acidified with ultra-pure HNO₃ to pH < 2and stored at 4°C prior to analyses. Sediments were collected using a grab sampler and analyzed for total extractable metals using the multi-acid digestion method. Particle size classification was done by standard method of analysis by sieving and organic carbon (OC) was estimated using the Loss on Ignition (L.O.I) method. Data obtained was tested for normality and homogeneity of variance. Heavy metal concentrations were compared using analysis of variance (ANOVA) to test for differences among sites ($\alpha = 0.05$). Pearson correlation was used to establish inter metallic relationships. Mean values of the physico-chemical parameters studied for all sites (pooled data) were as follows: E.C. 374.19±0.5µScm-1, pH 7.62±0.03, temperature 28.4±0.15°C, T.D.S. 373.6±0.5 and salinity 0.12±0.05%. There were significant differences between the sites for all parameters measured (p < 0.05) except for percent salinity (p = 0.739). The range mean concentrations of heavy metals in water were as follows Cu (0.4–0.7), Cd (0.6– 0.8) and Hg (0.003-0.005) ppb. The range of mean sediment concentrations (in mg/kg) were as follows: Cu (6.95-17.0), Cd (1.04-1.21), and Hg (0.18-0.27). Sites with higher percentages of silt and clay recorded a higher concentration of Cd and Cu same as to the percentage of TOC. Mean concentrations of heavy metals in water and sediments columns showed that a greater percentage of Cu (90.2 %) was retained in sediments while Cd and Hg released a greater percentage to the water column compared to what was in the sediment (36.8 % and 29.8%). Over 95% of the concentrations of Cd and Hg in water and sediments were significantly lower than those recommended by the WHO and USEPA as drinking water guideline values. The findings can be useful in policymaking with regard to environmental management and conservation of regional lakes facing similar challenges. Information on metal concentrations in the lake's freshwater can also be used in protecting human health. Further research on metal partitioning in water and sediments is recommended.

TABI	LE OF	CONTENT	'S
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DECLARATION AND RECOMMENDATIONii
COPYRIGHTiii
DEDICATION iv
ACKNOWLEDGEMENTv
ABSTRACT vi
TABLE OF CONTENTS vii
LIST OF TABLESix
LIST OF FIGURESx
LIST OF ACRONYMS AND ABBREVIATIONSx
CHAPTER ONE 1
1.0 INTRODUCTION1
1.1 Background information
1.2 Statement of the problem
1.3 Objectives
1.4 Hypotheses
1.5 Justification
1.6 Definition of terms
CHAPTER TWO9
2.0 LITERATURE REVIEW
2. 1 Introduction
2.2 Physico-chemical assessment of water quality
2.3 Sedimentation and its impacts
2.4 Heavy metals in water and sediments and their potential impacts on human and environmental health
2.5 Health effects of selected heavy metals and populations affected

2.6 Human activities affecting water quality in Lake Baringo in the catchment areas	22
2.7 Conceptual framework	
2.8 Scope	
CHAPTER THREE	29
3.0 MATERIALS AND METHODS	29
3.1 Study site description	29
3.2 Sediment sample collection and analysis	32
3.3 Water sampling and analysis for metals	34
3.4 Statistical analyses	34
CHAPTER FOUR	36
4.0 RESULTS	36
4.1 Physicochemical parameters of surface water	36
4.2 Heavy metal concentrations in water samples	37
4.3 Heavy metal concentration in sediments	40
4.4 Sediment characteristics (Grain size and TOC)	43
CHAPTER FIVE	45
5.0 DISCUSSION	45
5.1 Physico-chemical Parameters.	45
5.2 Heavy Metal Levels in Water	47
5.3 Heavy metals in sediments	49
5.4 Partitioning of heavy metals in water and sediment columns	50
5.5 Characteristics of sediments	53
CHAPTER SIX	56
CONCLUSIONS AND RECOMMENDATIONS	56
REFERENCES	58

LIST OF TABLES

Table 1: Size classification of sediments	15
Table 2: GPS coordinates of sampling sites	32
Table 3: Summary of statistical analysis used to test/analyse data	. 35
Table 4: Means (±SE) of various physicochemical variables in water samples	
collected from Lake Baringo	36
Table 5: TOC and grain size distribution of sediments in Lake Baringo	44
Table 6: Correlations between Cu, Cd and Hg and different grain sizes of sediments	44
Table 7: Water quality standards for various parameters by NEMA and WHO/USEPA	47
Table 8: Overall mean concentrations of heavy metals in water and sediments of Lake	1
Baring and the WHO set limits	52

LIST OF FIGURES

Figure 1: Conceptual framework	27
Figure 2: Map showing water and sediment sampling sites in Lake Baringo	31
Figure 3: Spatial variation of Cu concentration in water during the study period	38
Figure 4: Spatial variation of Cd concentration in water during the study period	39
Figure 5: Spatial variation of Hg concentration in water during the study period	40
Figure 6: Spatial variation of Cu concentration in sediments during the study period	41
Figure 7: Spatial variation of Cd concentration in sediments during the study period	42
Figure 8: Spatial variation of Hg concentration in sediments during the study period	43

LIST OF ACRONYMS AND ABBREVIATIONS

APHA:	American Public Health Association	
As:	Arsenic	
Cd:	Cadmium	
Cu:	Copper	
EC:	Electrical Conductivity	
Hg:	Mercury	
KMFRI:	Kenya Marine and Fisheries Research Institute	
MoH:	Ministry of Health	
NEMA:	National Environment Management Authority	
Pb:	Lead	
TDS:	Total Dissolved Solids	
UNEP/CEP:	United Nations Environmental Programme (Caribbean Environment Programme)	
USEPA:	United States Environmental Protection Agency	
WHO:	World Health Organization	
WRMA:	Water Resource Management Authority	

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background information

Management of natural resources such as water, soils and vegetation in semi-arid regions is an issue of concern in many countries. This is the case for Kenya where most of the population lives in the crowded areas of the country with moderate to high rainfall (Johansson and Svensson, 2002). In Kenya, arid and semi-arid land (ASAL) covers 80% of the country and around 30% of the population lives in those harsh ASAL areas (Johansson and Svensson, 2002). The rapidly growing human population has lead to the expansion of the agricultural activities to the semi-arid regions that are fragile and vulnerable to anthropogenic activities. The growing population, combined with limited land scarcity in the agriculturally productive highlands has led to increasing immigration to marginal areas in spite of their ecological limitations. But since those marginal and moisture deficit regions are vulnerable, to the increased population, the exerted pressure has often resulted in severe degraded land, soil erosion and sedimentation of open water bodies including lakes and rivers.

Lake Baringo is centred at 00°32'N 036°05'E and is Kenya's third largest freshwater lake in Kenya. It is internationally recognized for its biodiversity Ramsar Site no. 1159 (www.ramsar.org). The larger part of Lake Baringo watershed is characteristic of semi- arid environment and faces many challenges among which soil erosion (Onywere *et al.*, 2014) and water pollution is also high. These have deteriorating effects not only on the land resources, the soil productivity and the size of available agricultural land but also on open waters, as streams and lakes, through its detachment, transportation and deposition of sediments. The sediments and runoff by extension then become sources of contamination to most water bodies that serve as drinking water sources for many people living in the surrounding areas.

More recently there have been environmental impacts of far reaching dimension on both human and livestock health, brought about by an invasive plant species *Prosopis spp*. (Mathenge plant) introduced to the area to control erosion and provide fodder for livestock, the basis of livelihood in the area. The concerns on prosopis spp. are on lowered water table and a threat to the lake shoreline plants. In addition the area is a highly fragile ecosystem with impacts on water quality from geothermal manifestation. The drainage into Lake Baringo is via Molo River which collects water from the Mau Escarpment as far south as Elburgon Forest, and is structurally controlled, following the troughs between the fault scarps or the base of the fault scarps in its flow northward. It flows through the Loboi plain into the lake. Ndoloita hot springs are also controlled by the Ndoloita fault scarp, and take its waters into the Loboi Swamp on the northern end of Lake Bogoria. From the swamp the river flows north into Ngarua swamp where it joins the Molo, into Lake Baringo, 23 km north of Lake Bogoria. Perkerra River also provides significant recharge into the lake (Onywere *et al.*, 2014).

The increase in human population in the drainage basin of Lake Baringo has exerted pressure on the available water resources which has led to a decline in the quality and quantity of water and other resources within the lake. The number and population of urban centres in the lake's drainage basin have been on the rise over the years posing a threat to the lake's survival. It is subject to direct deposits mainly from sources such as anthropogenic activities, runoff, the atmosphere and erosion due to its exposure. Studies have shown that water quality can be negatively impacted by such activities and thus rendered unsafe for aquatic life and human use (Oduor, 2003; Ogendi *et al.*, 2007; Ogendi *et al.*, 2014).

Previously published records of the lake Baringo levels show significant rise and flooding of the mudflats and the ring of acacia forest around the lakes in 1901 and 1963. The flooding being witnessed during this study suggested a return of a 50 year cyclic climatic event (Onywere *et al.*, 2014). The increase in water volume has been significantly high and the input from the rivers recharging the lakes has been consistent, indicating that the flooded situation will not cease soon. The flooding has had immense and detrimental effects on the ecosystem, the settlements, the infrastructure and the biodiversity. Despite the recent rise in lake levels, some studies have shown that during the last decades both the depth and the area of Lake Baringo have decreased dramatically. For instance, a study by Johansson and Svensson (2002) reported that the shrinkage of the lake was due to both siltation and inadequate inflow of water volumes to the lake creating a negative water balance. The change in land-cover (for example deforestation) around the catchment area causes an increase erosion and sediment transport to the lake and changes in hydrologic pattern but that could be amplified by changed rainfall

conditions. Deforestation in the catchment area is on the rise mainly as result of extensive overgrazing, charcoal burning and expansion of human settlements. The changed land cover is in many respects an effect of the increased population combined with the large social importance of livestock.

The main town near the lake is Marigat, other smaller settlements include Kampi ya Samaki and Loruk. All these urban centres have contributed increased population density and enlarged spatial expansion over the last few decades. Lake Baringo contributes to the economy of the country as well as community livelihoods through tourism which is the major activity in this area and boating. The lake is threatened by irrigation activities through the abstraction of large volumes of water from both the lake and the inflowing rivers. For instance, Perkerra Irrigation Scheme utilizes over 70% of the Perkerra River water leaving 30% to flow into the lake (Oduor, 2003). Pastoralism and agro-pastoralism are also the major activities practiced by the residents including the Ilchamus, Rendille, Turkana and Kalenjin, threatening further the lake through sedimentation and increase in erosion. Lately the lake's water level has steadily increased leading to submergence of some of the infrastructure on its shores, crop failure and mass displacement of people and livestock (Lake Baringo, 2012).

Studies by Johansson and Svensson (2002), report that anthropogenic activities on the shores as well as on the drainage basin of Lake Baringo have led to the degradation of the lake and the land-water ecotone in the recent past. The lake basin is shallow and has no known surface outlet. The waters are assumed to seep through lake sediments into the faulted volcanic bedrock therefore serving as a sink for the contaminants emanating from anthropogenic activities. Heavy metals constitute some of the contaminants that are of major concern to human health workers, tourist entrepreneurs, wildlife, fisheries managers, and conservationists owing to their ability to accumulate in the lake sediments. Pollutants in the surrounding and/or underlying environments enter into water bodies and have been shown to affect aquatic life depending on their chemical speciation, toxicity, bioavailability, rate of uptake and metabolic regulation by specific organisms.

Studies on basic physico-chemical characteristics carried out in various rivers and lakes have focused on the water quality parameters with little or no consideration given to the bottom or sediment characteristics. Sediment analyses are carried out to evaluate qualities of the total ecosystem of a water body (Nnaji *et al.*, 2010). Studies point out that soils and sediments are repositories for physical and biological debris, and they are considered to be the ultimate sink for a variety of toxicants because pollutants may persist in sediments long after the original sources of contamination are eliminated. In the hydrologic systems, sediments serve as an indicator of contamination since it is a media for metal uptake and also due to their high sensitivity compared to water. Soares *et al.*, (1999), reported that sediments have the capacity to accumulate and integrate low concentrations of trace elements in water over time allowing the possibility for metal determination even when levels in overlying waters are extremely low and undetectable.

Increased metal loads in lake water and sediments are a human health concern due to bio-magnification of metals along the aquatic and terrestrial food chains and food webs. Human health risks are primarily due to the elevated concentrations of copper, cadmium, lead and mercury in water and fisheries that are part of the local people's diet. For instance, Cadmium has been linked to kidney and liver damage as well as osteoporosis and pulmonary emphysema as was the case in Japan where people consumed rice cultivated using cadmium-contaminated irrigation water (Dipankar *et al.*, 1999). The goal of this study was to determine the physicochemical parameters of water and the characteristics of sediments. Additionally, the study sought to assess the sources and the concentration of heavy metals in water and sediments on a spatial scale on Lake Baringo.

1.2 Statement of the problem

The presence of inorganic and organic pollutants including heavy metals in Lake Baringo is an issue of concern as their presence impairs the water quality. This in turn affects the health of human who consume the metal contaminated water and fish. Communities that live within the basin of the Lake Baringo (Tugens, Pokots and Illchamus) depend on the lake as a source of water for various purposes (drinking, cooking and agriculture). Local regulations aimed at improving the quality of freshwater ecosystems have been important steps in achieving improved ambient water quality conditions. The area has been experiencing high rates of sedimentation caused by the increased soil erosion impairing sediment quality. However, the sediments of aquatic ecosystems have not received this same attention. This is surprising and unfortunate, as sediments and the associated benthic organisms are critically important in maintaining the health and productivity of aquatic ecosystems. In a healthy aquatic community, sediments provide a habitat for many organisms but with increased sedimentation, the interstices of gravel and cobble stream bottoms, greatly decreasing the spawning areas for many fish species and the habitat for macroinvertebrates, which serve as food for many fish species. Sediments carry along with them organic matter, animal or industrial wastes, nutrients, and chemicals. Due to the different land use activities carried out in the area, the sediments transported also may contain some toxic substances such as pesticides which may contain heavy metals and depending on their properties, such as toxicity, solubility and chemical breakdown rate they may pose a greater danger to aquatic plants and animals and eventually to human health. Presence of heavy metals in a water body affects the quality of water and sediments which therefore impact the aquatic organisms from the macroinvertebrates to fish of which through biomagnifications, the health of humans especially those who consume fish (food fish) are at risk.

1.3 Objectives

1.3.1Broad Objective

The overall objective was to investigate the influence of anthropogenic activities and sediment characteristics on water and sediment quality in Lake Baringo.

1.3.2 Specific Objectives

- 1. To determine the physico-chemical characteristics of water at selected sites of Lake Baringo.
- 2. To characterize the sediments (grain sizes) of lake Baringo study sites and total organic matter.
- 3. To quantify the concentration of selected heavy metals in lake water and sediments from selected sites of Lake Baringo (Pb, Cu, Cd and Hg) and compare with the recommended WHO/EPA values.

1.4 Hypotheses

- 1. There is no significant difference in physico-chemical variables of lake water irrespective of anthropogenic disturbance levels.
- 2. Sediment characteristics (grain size) and organic matter is the same among the selected sites.
- 3. There is no significant difference in the concentration of heavy metals in lake water and sediments collected from the different sampling points and their concentrations are within the range recommended by WHO/EPA.

1.5 Justification

Pollution in aquatic ecosystems by inorganic chemicals is a major threat to the aquatic organisms including fishes. Runoff water containing pesticides and fertilizers and effluents of industrial activities and sewage effluents have been cited as the main sources of heavy metals (Saeed and Shaker, 2008). The most common anthropogenic sources of metals are industrial, petroleum contamination and sewage disposal. As mentioned earlier, Lake Baringo is a fresh water lake which is important to the population of its drainage basin as a source of water for domestic use and for watering livestock, a source of fish (food fish) for the local community, a source of vegetation products which are used in boat construction and also of great economic value through tourism and the conservation of biodiversity. The high dependence on the water body has led to decline in the water levels as well as deterioration in water quality. Pollution in this lake is attributed to agricultural and horticultural as well as domestic and industrial activities in the lake's catchment. The heavy metal pollution is exacerbated by the haphazard solid and liquid waste disposal practices from the surrounding urban centres.

Pastoralists in the area also keep large herds of cattle which overgraze the catchment vegetation leading to enhanced runoff, soil erosion and sedimentation in streams and the lake. The sediments are considered to be the ultimate sink for a variety of heavy metals and other toxicants which can affect the survival of aquatic organisms.

Elevated heavy metal levels can cause adverse effects not only to aquatic organisms but also terrestrial organisms like humans that utilize water and food items from the lake. Heavy metals from the sediments make their way into the food chain, accumulating in fish, water birds and other wildlife. The fact that human and environmental health is likely to be negatively affected through consumption of heavy metal-contaminated fish justifies this study. We need to have adequate information on the levels, sources and likely effects of heavy metals in the lake. The study specifically identified the potentially toxic metals; quantified their concentrations in the water and sediments at some selected sites in the lake and related them to the WHO/EPA guidelines.

The information obtained can be used by relevant institutions such as NEMA, KMFRI, WRMA, MoH and managers of the lake among others in the management and conservation of such water bodies, and in issuing fish and water consumption advisories and therefore preventing humans from the adverse effects of consuming heavy metal-contaminated water and fish. Such information can also greatly contribute to a comprehensive environmental policy for water bodies receiving metal pollutants from adjacent areas.

1.6 Definition of terms

Electrical Conductivity: It is a measure of the flow of electric current in water due to the presence of ions. It gives an estimation of the amount of Total Dissolved Solids (TDS) or the total amount of dissolved ions in the water.

Reference site: a specific locality on water body that is undisturbed or minimally disturbed and is representative of the expected physical and chemical characteristic of other localities on the same water body or water courses.

Sedimentation: it is the process of allowing particles in suspension in water to settle out of the suspension under the effect of gravity.

Surface water: A term commonly used to designate the water in lakes, marshes, glaciers, and reservoirs as well as that flowing in streams. In the broadest sense, surface water is all the water on the surface of the Earth.

Total organic Carbon: It is the amount of carbon bound in an organic compound and is often used as a non-specific indicator of water quality.

Total Solids: Refers to the matter suspended or dissolved in water or wastewater.

Water quality: Refers to the condition of being in a suitable state physically, chemically and biologically as to render water fit for humans and aquatic life.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Introduction

Aquatic systems can be polluted due to natural causes but also it can be attributed to human and animal activities such as discharges of domestic or industrial effluents, leaching and runoff of pesticides in agricultural lands (Ferreira, 2012). Pollution of the aquatic environment by inorganic and organic chemicals is a major factor posing stress to the biotic community thereby threatening the survival of aquatic organisms. The aquatic environment with its water quality is considered the main factor controlling the state of health and disease in animal and man (Saeed and Shaker, 2008). Currently, there is an increase in the use of the waste chemical and agricultural drainage systems representing the most dangerous chemical pollution and, their levels may be elevated as a result of increased input into the lakes resulting from industrial activities (Ferreira, 2012).

Extensive research on five Rift Valley lakes, including Lake Baringo was carried out to determine heavy metal concentrations in water and surface sediments by Ochieng *et al.*, (2007), to assess the recent increases in anthropogenic activities. The temporal physico-chemical parameters in Lake Baringo by Odada *et al.*, (2008) and by Ouma and Mwamburi (2014), where the parameters were within maximum allowable concentrations and guidelines by WHO (1993).

2.2 Physico-chemical assessment of water quality

In order to know the tropical status of an aquatic ecosystem, a study of the physicochemical parameters is essential and fundamental. The physico-chemical characteristics of an aquatic environment directly influence the life inhabiting it by the distributional patterns and species composition (Lashari *et al.*, 2009; Koffi *et al.*, 2014). In aquatic habitats, environmental factors include various physical properties of water, such as solubility of gases and solids, light penetration, temperature and density. The chemical factors such as pH, hardness, phosphate and nitrate are very important for growth and dispersal of the phytoplankton on which zooplankton and higher consumers depend for their existence (Lashari *et al.*, 2009). Changes in these constituents often create an adverse environment to organisms, limiting their growth and interfering in the physiological processes, thereby reducing their ability to compete with other populations within the environment, ultimately resulting to a change in that community structure (Harney *et al.*, 2013). The above stated parameters vary with depth of water and also along the length and the breadth of the lake. The spatial variations of the water quality parameters are due to many physical factors including wind action and solar radiation (Mazumdar *et al.*, 2007).

2.2.1 *Temperature*

Temperature is an important parameter in terms of its effect on aquatic life. In the aquatic ecosystems, changes in temperature are evident seasonal patterns. Its influence on limnological phenomena such as stratification, gas solubility, pH, conductivity and planktonic distribution are well known (Lashari *et al.*, 2009). Temperature measurements are useful in indicating trends for various chemical, biochemical and biological activities. An increase in temperature leads to faster chemical and biochemical reactions and reduce the solubility of gases (Lashari *et al.*, 2009; Harney *et al.*, 2013). Water temperature also regulates to some extent the growth and death of microorganisms and the kinetics of the biochemical oxygen demand. The water temperature also influences all the metabolic and physiological activities of life processes. It is an important parameter in the calculation of oxygen solubility and carbon dioxide and bicarbonate and carbonate equilibrium. Study by Mazumdar *et al.*, 2007 shows that surface temperature of water of the lake on a particular day also varies over different spatial locations, besides variation over depth at a given site. The temperature near the banks (littoral zone) is always higher than that at the mid-reach.

Temperature exerts an important effect on metal speciation, because most chemical reaction rates are highly sensitive to temperature changes. Temperature may also affect quantities of metal uptake by an organism due to the biological process rates (John and Joel, 1995). According to Fritioff *et al.*, (2005), the solubility of metals in water is not affected by the seasonal variation in water temperature. However, cool water contains more dissolved oxygen than warm water thus making the metal concentration in the interstitial water of the sediment decrease with decreasing temperatures. This is because at high redox potentials, more metals are bound to sediment colloids compared to the low redox potentials

2.2.2 *pH*

It is the measure of the acidity or alkalinity of an aqueous solution. pH is considered as an important ecological factor and is the result of the interaction of various substances in solutions in the water (Harney et al., 2013). The presence or absence of free carbon dioxide and carbonate and planktonic density leads to the various changes in pH in an aquatic ecosystem. The high pH results in high photosynthetic activity due to the abundance of the algal population. The pH is an important factor for the growth of aquatic vegetation. It is well documented that pH is directly related to carbonates and inversely related to free carbon dioxide (Lashari et al., 2009). Among biotic factors, high photosynthetic activity due to increased production of phytoplankton may support an increase in pH. Changes in the pH of water bodies can have a drastic effect on aquatic life as these organisms have adapted to live in water of specific pH and even slight changes may result in death leading to a loss in aquatic biodiversity (Igbinosa et al., 2012; Idowu et al., 2013). Ochieng et al., (2007) recorded pH values of Lake Baringo to range between 8.25 \pm 0.31–8.65 \pm 0.44) and attributed this range to the presence of carbonates and bicarbonates derived from the carbonatite volcanic rocks. Odada et al., (2008) also recorded pH values in 2001 to range between 8.8 - 9.1. The high pH values are because of the alkaline hotspring discharge from Ol Kokwa Island which is located in the lake.

In aqueous solutions, pH is an important factor governing metal speciation, solubility from mineral surfaces, transport, and eventual bioavailability of metals (John and Joel 1995; Koffi *et al.*, 2014). It affects both solubility of metal hydroxide minerals and adsorption-desorption processes. Most metal hydroxide minerals have very low solubility under pH conditions in natural water. Because hydroxide ion activity is directly related to pH, the solubility of metal hydroxide minerals increases with decreasing pH, and more dissolved metals become potentially available for incorporation in biological processes as pH decreases (Başyiğit and Özan, 2013).

2.2.3 Electrical Conductivity (EC)

Electrical conductivity is an estimate of the amount of Total Dissolved Salts (TDS) or the total amount of dissolved ions in the water. Sources of dissolved ions include soil and rocks in the watershed, wastewater from sewage treatment plants, agricultural runoff, and urban runoff from roads. Natural water has low conductivity, but contamination increases the levels of conductivity. In Lake Baringo, Odada *et al.*, (2008) recorded conductivity values to range between 1.39 - 1.67 mS/cm which indicated the sub-salinity of the lake. One of the important criteria usually used to assess the irrigation water quality is total concentration of dissolved salts and is expressed in terms of electrical conductivity.

2.2.4 Dissolved oxygen (DO)

Dissolved Oxygen levels are considered as the most important and commonly employed measurement of water quality and indicator of a water body's ability to support desirable aquatic life. Like terrestrial animals, fish and other aquatic organisms need oxygen to live. As water moves past their gills (or other breathing apparatus), the DO is transferred from the water to their blood. The oxygen supply in water mainly comes from two sources atmospheric diffusion and photosynthetic activity of plants (Lashari *et al.*, 2009; Idowu *et al.*, 2013). The rate at which oxygen diffuses in water is slow. The quantity of dissolved salts and temperature greatly affect the ability of water to hold DO.

The solubility of DO increases with decreasing temperature (Lashari *et al.*, 2009). In Lake Baringo, Oduor *et al.*, (2003) recorded Oxygen concentration above 6 mg 1^{-1} (over 78% of relative saturation). Njiru (2012) recorded DO levels in Lake Victoria to have a maximum of 11.3 mg/l in the littoral stations and in lower depth (<30 m) levels of less than 1 mg/l were measured. Occurrence of frequent fish kills in the lake has been attributed to increased development of anoxia in the water column (Njiru, 2012). Anoxic levels in lakes result mainly from increased bio-degradation of organic matter and stratification, which hinders re-oxygenation of hypolimnion (Wetzel, 2001).

Dissolved Oxygen is important in the precipitation and dissolution of organic substances in water. When the values of DO are high, during the rainy season they are mainly attributed to low temperature and high photosynthetic activities and low values of DO during dry seasons attributed to high temperature and high rate of oxidation of organic matter (Harney *et al.*, 2013). Turbidity affects the levels of dissolved oxygen indirectly by limiting photosynthesis through the reduction in light penetration (Omondi *et al.*, 2014). The DO content has the possibility of affecting the rate of oxidation of organic compound thus improve the release of the metal.

2.3.5 *Turbidity*

Turbidity in water is caused by the presence of suspended matter such as clay, silts, finely divided organic and inorganic matter, plankton and other microscopic organisms. Silt gives the advantage that it checks light penetration in certain area of the Lake, including the inlets. Excessive turbidity in surface waters, destined for human consumption can cause potential problems for water purification processes such as flocculation and filtration, which may increase treatment costs. Chlorination can never be an effective disinfectant in the presence of suspended matter in water, which provides a sanctuary for various pathogenic organisms however. There may also be a tendency for an increase in trihalomethane (THM) precursors, when highly turbid waters are chlorinated (Igbinosa *et al.*, 2012). It is therefore a prerequisite that reasonably safe and wholesome drinking water must have very low turbidity to qualify as first class water in any domestic water supply system.

Elevated turbidity values during the raining period could be attributed to increased surface runoff and erosion, through rain falls. The high rates of sedimentation in Lake Baringo have lead to an increase in turbidity thus the water quality has been affected. The turbidity values recorded ranged between 350-900 NTU which are high values. Reduced water transparency is related to increased turbidity which was less that 0.1 m as measured by secchi disc (Odada *et al.*, 2008)

Organic and inorganic particles cause the scattering of light in water resulting to turbidity. Wind action leads to the re-suspension of sediments leading to low transparency in the water column. This is a major physical factor in such ecosystems as it affects the abiotic and biotic variables. Low transparency inhibits the penetration of light this reducing the euphotic zone. This minimizes the primary production therefore having cascading effects up the food web and ultimately affecting the fisheries production (Omondi *et al.*, 2014). Particulates also provide attachment sites for heavy metals and many toxic organic contaminants such as PCBs, PAHs and many pesticides.

2.3 Sedimentation and its impacts

Sediment is natural earth material. It consists of soil particles of all sizes ranging from the smallest, "silt (mud) and sand", to larger sizes which include the gravels, cobbles and boulders. Sediment also includes extremely hard and very large materials (bedrock) and very small tightly compacted materials (clay). All of these materials succumb to the forces of erosion from water, wind and pressures caused by expanding and contracting forces. A stream contains a certain variety of sediment based upon its geology, topography, precipitation rates and other factors in the watershed. Decomposition of plants, animals and soil erosion are the major sources of sediments. These sediments particles end up in the rivers, lakes and streams through the transportation by wind, water and ice. Sediment strata serve as an important habitat for the benthic macroinvertebrates whose metabolic activities contribute to aquatic productivity (Ansa and Francis, 2007; Singare *et al.*, 2011).

Sediment input in water bodies may impact the aquatic communities either directly or indirectly for example by reducing light penetration, smothering, reducing the habitats and by introduction of absorbed pollutants (pesticides, metals, nutrients). Lokhande *et al.*, (2011), reported that particulate matter became associated with most of the metal compounds, hydrophobic organic contaminants and nutrients which end up in water bodies and accumulated in the bottom sediments. The main environmental threat to Lake Baringo is sedimentation. It reduces both the depth and the surface area of the lake, in addition to destroying the habitats of aquatic animals. The parts of the catchment that produce the most sediment are the steep slopes with erodable soils. Such areas include the foot slopes of Tugen Hills around Cheberen and Tenges. The eroded soils are deposited on the flat lower reaches of the drainage basin and in the lake (Odada *et al.*, 2006).

UNEP/CEP (1994) and Castro and Reckendorf (1995) reported that increase in fine sediment in gravel-bed streams has been interpreted by fishery biologists as having an adverse effect on fisheries. Sedimentation cause damage to fish by irritating or scouring their gills and degrade fish habitats as gravel containing buried eggs becomes filled with fine particles, thus reducing the amounts of oxygen available for their survival. It also reduces the success of visual predators and may also harm some benthic macroinvertebrates. Once the sediments are contaminated they cause, tumors, rotting of the fins and even genetic mutations in fish. Fine sediments also adsorb many toxic organic chemicals, heavy metals and nutrients physically and/or chemically, therefore an increase of fine sediment load into the aquatic environment leads to increased deposition of these toxic substances that result in further negative impacts such as eutrophication.

External environmental factors such as pH, dissolved oxygen, electrical conductivity and the available surface area for adsorption caused by the variation in grain size distribution determines the accumulation of metals from the overlying water to the sediments (Barakat *et al.*, 2012; Koffi *et al.*, 2014). However, metals cannot always be fixed by sediments permanently since some metals which are sediment-bound can remobilize and be released back to waters through the variation of environmental conditions. These include acidification, redox potential conditions, and organic ligand levels and impose adverse effects on living organisms (koffi *et al.*, 2014.)

2.3.1 Characteristics of sediments

2. 3.1.1 Sediment size

Sediment particles size is an important characteristic as it affects their entrainment, transport and deposition, and therefore provides important clues to the sediment provenance, transport history and depositional conditions (Maslennikova *et al.*, 2012). Grain sizes can vary over several orders of magnitude. Grain size usually refers to grain diameter and is reported as millimeters (mm), micro-meters (microns) or phi" units (\emptyset) (Harris, 2003). Table 2 shows the particle size classifications.

Table 1: Size classification of sediments.

Туре	Size range (mm)
Gravel	>2
Sand	0.063 - 2
Silt	0.004 - 0.063
Clay	< 0.063

(Source: Harris, 2003).

The physical and chemical properties of sediments, (grain size, surface to volume ratio, heavy metal contents of the main geochemistry phase), are the main factors that influence heavy metal content in sediments in which grain size is a main control parameter (Zhu *et al.*, 2006; Jernström *et al.*, 2010; Maslennikova *et al.*, 2012). It is believed that coarse sediments contain a lower concentration of heavy metals than finer sediments ones. The main reason is that smaller grain- size particles have a larger surface-to-volume ratio. However, some studies have indicated that coarser particles shows a similar or even higher heavy metal concentrations than finer ones and the residence time of coarser particles are possibly responsible for higher metal content in the coarser size fractions (Jernström *et al.*, 2010; Maslennikova *et al.*, 2012).

The aquatic ecosystems health is also determined by the ability to support biodiversity. Different sediment particle sizes affect the survival rates of the different types of macroinvertebrates. Experiments carried out by Donohue and Irvine (2003) shows that their survival rates decreases with decreasing sediment particle size. Some macroinvertebrates such as gastropods feeding behaviours are affected significantly by sediment particle size, showing increasing severity of impact with decreasing particle size.

Grain size is also associated with the availability of contaminants associated with sediment grain size. Fine grain sediments tend to be higher in clay content and they contain higher levels of organic carbon, which is an indication of high bacterial activity. Fine sediments in aquatic ecosystems are also often associated with anoxic, high sulphide, high ammonia conditions as well as elevated metals and organic contaminants associated with the high organic content. Bioturbation of fine sediments has the potential of causing high mortality rates in organisms, and also cause the disassociation of many compounds from sediments, increasing their bioavailability and toxicity (Duckworth *et al.*, 2000).

2. 3.1.2 Sediment Organic Matter

Organic materials can be derived from decomposition of land plants, mangroves, macrophytes, algae, phytoplankton, zooplankton, and bacteria. The composition of the buried organic matter found in sediments therefore varies greatly due to their different inputs (Hedges and Keil, 1995). Different areas are classified according to the amount and composition of the buried organic matter such as lakes, delta zones, and continental margins among others.

Organic matter control the distribution of trace elements such as mercury in soil and, suspended and bottom aquatic sediment therefore, the measurement of the Total Organic Carbon present in the organic matter is an important parameter (Hedges and Keil, 1995; Goodarzi and Sanei, 2006). The capacity of organic matter to concentrate trace elements however, varies with the amount and type of organic matter. Various factors that affect the ability of organic matter to concentrate elements include chemical and physical factors such as large surface area, high cation - exchange capacity and high negative ability.

Many studies have described the chemical relationship between organic matter and trace elements at the molecular level. These studies have focused primarily on the role of organic complex materials, such as humic substances in concentrating trace elements during geochemical processes in sediments. Little research has been done on physical geochemical aspects of organic matter as a substrate for trace elements. Aquatic organic matter in recent sediment is found as either surface coatings or separate organic particles and debris. The organic matter present in the form of surface coatings provides a larger surface area since it is able to concentrate on the small sediment size fractions leading to the accumulation (Goodarzi and Sanei, 2006).

2.4 Heavy metals in water and sediments and their potential impacts on human and environmental health.

Heavy metal pollution, owing to its permanent existence and biological enrichment, has long been an important subject in the field of international environmental science (Jernstrom *et al.*, 2010; Maslennikova *et al*, 2012). With respect to the protection of human health, contaminated water and sediments represents a significant environmental concern. Humans can be directly exposed to contaminated water and sediments through primary contact recreation, including swimming and wading in the affected water bodies. In addition, indirect exposures to sediment-associated contaminated due to bioaccumulation in the food web (Ingersoll and MacDonald, 2002; Koffi *et al.*, 2014). Presence of inorganic chemicals is a form of pollution in the aquatic environment which has been considered a major threat to the aquatic organisms. Drainage of water containing pesticides and fertilizers resulting from the various agricultural activities and effluents of industrial activities and runoffs in addition to sewage effluents supply

the water bodies and sediment with huge quantities of inorganic anions and heavy metals (Saeed and Shaker, 2008).

Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring its concentration in water, sediments and biota which generally exist in low levels in water and attain considerable concentration in sediments and biota. Heavy metals do not exist in soluble forms for a long time in waters; they are present mainly as suspended colloids or are fixed by organic and mineral substances (Ebrahimpour and Mushrifah, 2008).

Metal ions can enter the food chains and be concentrated in aquatic organisms to a level that affects their physiological state. Heavy metals are the effective pollutants of great concern having drastic human and environmental impact on all organisms. Some trace metals (such as Zn, Cu and Fe) play a biochemical role in the life processes of all aquatic plants and animals; therefore, they are essential in the aquatic environment in trace amounts (Saeed and Shaker 2008). However, heavy metals, including both essential and non-essential elements, have a particular significance in eco-toxicology, since they are highly persistent and all have the potential to be toxic to living organisms (Ebrahimpour and Mushrifah, 2008). In Lake Baringo, the potential source of Cu and Hg are industrial wastes as well as algaecides, while that of Cd is the phosphatic fertilizers used in crop farms.

Lake sediments are normally the final pathway of both natural and anthropogenic components produced or derived to the environment. Sediment quality is a good indicator of pollution in water column, where it tends to concentrate the heavy metals and other organic pollutants (Soares *et al.*, 1999; Kamau *et al.*, 2007; Ebrahimpour and Mushrifah, 2008; Saeed and Shaker, 2008).

Metal-contaminated waters and sediments serve as sources of metals that can cause lethal and /or sublethal effects to stream macroinvertebrates as well as fish and other higher organisms through food chain transfer. Increased metal concentrations significantly reduce water and sediment quality which may lead to "fish kills", reduced survival and growth of macroinvertebrates and decreased taxa richness of other benthic macroinvertebrates (Ogendi *et al.*, 2007; Ogendi *et al.*, 2008). Some studies on Lake Baringo have shown that birds may adversely be affected by consuming prey items that contain heavy metals (Odada *et al.*, 2008) and for this reason it is important to assess levels of heavy metals in sediments as they are a habitat for the aquatic organisms. Related studies indicate increasing levels of heavy metals in water and sediments are characterized by intensive agricultural and industrial activities on the drainage basin (Kamau, *et al.*, 2007; Ochieng *et al.*, 2007).

In freshwater ecosystems, the largest pool of methylmercury (MeHg) is found in fish tissues. MeHg being a neurotoxicant, the health of natural predators of fish (including humans) can be affected by fish consumption. It generally has been considered that piscivorous animals are at the top of aquatic food chains, and thus contain the highest amount of MeHg (Sarica *et al.*, 2005). Other studies have shown that the most common form of prenatal exposure to mercury is maternal fish consumption that caused premature births and neurodevelopment disorders among children (Ogendi *et al.*, 2007).

Elevated Cd levels have been shown to be detrimental to survival, growth and reproduction of cladocerans, fish and birds (Dipankar *et al.*, 1999). Lead (Pb), is a non-specific poison affecting all body systems of various organisms. Increased metal loads in lake water and sediments are also a human health concern due to biomagnification of metals along the aquatic and terrestrial food chains and food webs. Overall, human health risks are primarily due to the elevated concentrations of Cr, Pb, Cd, As, and Cu in water and fisheries that are part of the local people's diet. Consumption of arsenic-laden water and food crop rice in Southeast Asia including Bangladesh, India and the Bengal region in general has been linked to several health conditions such as cancer of the skin, kidneys, bladder, and lungs (Dipankar *et al.*, 1999; Mandal *et al.*, 1999). Kidney and liver damage as well as osteoporosis and pulmonary emphysema has been linked to Cd as was the case in Japan where people consumed rice cultivated using cadmium-contaminated irrigation water (Dipankar *et al.*, 1999; Mandal *et al.*, 1999).

2.5 Health effects of selected heavy metals and populations affected

a) Lead

Lead at high levels of exposure induces the development of anaemia. Children may die from the neurological effects of lead without even developing anaemia. Acute effects of lead on the central nervous system (CNS) are generally seen in children heavily exposed from pica and are manifest by severe encephalopathy which can culminate in coma and death. It is this issue which is of most concern in the environmental toxicity of lead because these effects have been reported to occur in children from the general population subjected to commonly occurring exposure regimes. Further concern relates to the greater susceptibility of children to lead resulting from the higher intake and uptake together with the greater sensitivity of the developing CNS (Hutton, 1987).

The major study relevant to this issue was carried out on children in the USA by Needleman *et al.* (1979) using dentine lead as the index of exposure. It involved numerous tests of performance and intelligence in the children, classified according to their dentine lead levels. The classroom behaviour of the children was rated by the teacher. The study reported that children from the high lead group showed significantly lower verbal IQ and performed less well on other behavioural tasks, after controlling for five covariates in an analysis of covariance. In addition, the teacher's assessments of classroom behaviour were reported to show a dose-dependent increase in poor ratings (Hutton 1987).

Since the Needleman study, other investigations in children from the Federal Republic of Germany (Winneke, 1983) and the United Kingdom (Yule and Landsdown, 1983) have reported an association between increased lead exposure and decreases in measurements of intelligence and behaviour.

b) Mercury

Methylmercury intoxication is characterized by effects on the CNS and the areas mainly affected are those associated with the sensory, visual and auditory functions and those concerned with co-ordination. Early effects are paraesthesia in the tongue, lips and distal extremities, while in more severe cases, blurred and constricted vision and ataxia may appear. The developing nervous system of the foetus is more sensitive to methylmercury than the adult and pre-natal exposure can result in neurotoxic effects in the infant in the absence of effects in the mother (WHO, 1976). Pregnant women are apparently more sensitive to methylmercury than are other adults. In the last thirty years, there have been several outbreaks of methylmercury intoxication of two distinct types. The Minamata disease, took place in Japan in the 1950s and 1960s was the first and it was caused by long-term ingestion of contaminated fish. There is disagreement over the number of poisonings caused by Minamata disease but one study estimates about 1000 cases, 3300 suspected cases and about 100 deaths (Tsubaki *et al.*, 1978).

Studies were carried out to examine the health of various communities of Canadian Indians because of their elevated methylmercury intakes from fish. The Methylmercury Study Group, 1980 reported an association between several neurological parameters and methylmercury exposure. Other populations with heavy fish consumption have also been identified in the Mediterranean, particularly in Italy, in Papua New Guinea, Peru, New Zealand and the Seychelles (WHO, 1976). In some of these areas no health-related studies have been undertaken, or they are currently still under way. Those studies which have been completed have failed to provide clinical evidence of methylmercury intoxication.

The other type of intoxication is characterized by the Iraqi epidemic in 1971-72 where exposure resulted from consumption of bread prepared from grain dressed with alkylmercury fungicides. The incident resulted in the poisoning of about 6000 individuals and the deaths of over 500 in hospital (Bakir *et al.*, 1973). Previous outbreaks of this type together with the number of poisonings are as follows: Iraq (1956), about 100; Iraq (1960), about 1000; Pakistan. (1969), about 100; Guatemala (1963-65), about 45; and Ghana (1967), about 150 (Hutton 1987). Clearly the inadvertent ingestion of seed treated with organic mercury as a fungicide is a hazard, despite a coloured dye being used and seed bags being marked in several languages.

c) Cadmium

The kidney is the critical organ of intoxication after long-term exposure to cadmium. One of the initial signs of renal dysfunction is an increased urinary excretion of proteins. Cadmium-induced proteinuria is generally considered to be characterized by the excretion of low molecular weight proteins. Until recently, reports of health effects of cadmium in populations not occupationally exposed to cadmium were confined to Japan. Many areas of Japan are contaminated with cadmium, as a result of discharges from numerous non-ferrous metal mines and smelters. Long-term consumption of rice grown in these areas has resulted in elevated cadmium exposure and signs of renal dysfunction in several localities (Hutton 1987). A syndrome termed 'itai-itai disease' has also been identified in one area characterized by severe renal dysfunction and damage to bone structure. The disease predominantly affected elderly multiparous women with poor nutritional status, who had lived in the contaminated area for many years.

A recent investigation also examined elderly females (>60 years) from a city in Belgium subjected to long-term cadmium contamination (Roels *et al.*, 1981). These women were reported to have larger cadmium burdens and a higher prevalence of signs of renal dysfunction compared with controls from a city with lower levels of cadmium contamination. The cadmium exposure levels in this population were much lower than those encountered in contaminated areas of Japan and the corresponding signs of renal dysfunction were also less pronounced. This study suggests that cadmium may exacerbate the age-related decline in renal function at moderate exposure levels to the metal.

The mortality statistics of the two Belgian cities have also been examined (Lauwerys and De Wals, 1981). Overall mortality rates were similar in the two populations but mortality from nephritis and nephrosis was higher in the cadmium 'polluted' city. However, mortality rates from uremia were similar in the two populations, a surprising finding given the apparent disparity in mortality rates from nephritis and nephrosis.

Mortality studies carried out in cadmium-contaminated areas of Japan have produced conflicting results. One investigation (Nogawa *et al.*, 1981) of a small population reported a significant increase in overall mortality for males with proteinuria. As in the Belgian study, this population was reported to show a large excess of deaths due to nephritis and nephrosis.

2.6 Human activities affecting water quality in Lake Baringo in the catchment areas

a) Deforestation, agricultural expansion and sedimentation

Deforestation, particularly of upper catchment areas of Lake Baringo, has led to increased runoff carrying greater sediment loads into the inflowing rivers and the lake systems. Sedimentation is considered the major threat as it reduces the depth and surface area of the lake

in addition to destroying the habitats of aquatic animals. The parts of the catchment that produce the most sediments are the steep slopes with erodable soils. Such areas include the foot slopes of Tugen Hills around Cheberen and Tenges. The natural forest in this region also has been exploited for timber, wood fuel and settlement. The benefits being lost as a result of deforestation include the functioning of the forest as a moisture reservoir: forests store 100 times more water than grasslands, capture air moisture and increase the incidences of rainfall, regulates river flows and prevents flooding, reduce the sediment load in river water, and regulate rainfall patterns. The Lake Baringo drainage basin has lost more than 50% of its natural forest cover, decreasing from 829 km² in 1976 to 417 km² in the 2001. Thus, the same proportion of the benefits derived from the forests also has been lost (Odada *et al., 2006*).

Deforestation facilitates the accumulation of greenhouse gases, such as carbon dioxide in the atmosphere. These gases can cause global warming and, hence, higher atmospheric temperatures. Increased air temperatures can lead to increased evaporation from the lake, resulting in a reduced water level in the lake. Overall, the potential effects of climate change on Lake Baringo are not yet well understood, due to a lack of reliable data.

b) Water pollution

Build up of sediments, agricultural runoff, domestic and industrial effluents are the main sources of water pollution in lake Baringo. The use of pesticides for agricultural purposes and against human pest vectors (e.g. tsetse fly) is an emerging problem for species survival and water quality in the lake. Mining activities in the catchment areas release pollutants (such as Pb, Cd, Fe, and Cu) and organic wastes from leaking sewage systems can accumulate in rivers and the lake which will affect water quality and species survival. Bioaccumulation of metals in the macroinverterbrates and fish may become a health problem in the future as population, uncontrolled effluent discharges and intensive agriculture increases. Sewage and runoff from farms, farmlands and gardens can contain nutrients, such as nitrogen and phosphorus, that cause excessive aquatic plant growth, and this in turn has a range of damaging ecological effects (Awange et al., 2013).

Emissions from factories and vehicles are released into the air. They can travel long distances before falling to the ground, for instance in the form of acid rain. The emissions create acidic conditions that damage ecosystems including forests and lakes. The pollution that passes directly into water from factories and cities can be reduced through treatment at source before it is discharged. It is harder to reduce the varied forms of pollution that are carried indirectly, by runoff, from a number of widely spread non-point sources, into freshwater and the sea (Mireri, 2005).

c) Water extraction and transfer

Throughout history, human activities have severely affected the condition of freshwater ecosystem. Surface water and groundwater are being degraded in almost all regions of the world including Lake Baringo by intensive agriculture and rapid urbanization. This has led to an increase in water transfers from water-rich catchments to those where water is limited with major implications for channel integrity and ecological functioning, and leading to a frequent loss of biodiversity. Water transfers produce: flow reduction in the donor rivers and increased flow in the recipient rivers; changes in the physical and chemical status of river's water; introduction of fine sediments from one river to another leading to a loss of benthic habitats such as gravel spawning beds for fishes; and spread of alien fish species, floating aquatic plants, and animal diseases and their vectors (Johansson and Svensson, 2002).

To meet the needs of the increasing population, sustain long-term human welfare, and conserve functioning ecosystems that provide us with the wide variety of goods and services we depend on, consumption of renewable natural resources must stay within the limits of biological capacity over the long term. By sector, the highest water use is for agriculture for irrigation followed by domestic use and industrial use (Odada *et al.*, 2006).

d) Development and dams

The dams are meant to accumulate water for irrigation, and for rural and urban water supply. For example, the Kiradich Dam, which covers an area of 2 km^2 on the Endao River, supplies water to the town of Kabarnet. Other dams include Chemeron Dam (area of 1 km^2), which is used for irrigation. Water diversions for irrigation also have been made from the

Perkerra, Molo and Ol Arabel Rivers. These water abstractions also have contributed to reduced stream flows. Both the lake and its rivers have been used throughout their history to water animals at various points. Therefore, the decreased water levels have significant impacts, especially on the livelihoods of the communities living downstream. This problem is likely to continue as long as the population in the upper catchment continues to increase.

e) Invasive species

The introduction of alien species in Lake Baringo area (*Prosopis juliflora*) can have a profound and devastating impact upon an ecosystem. It is a fast-spreading shrub with hairy evergreen leaves. It was introduced in 1982 and has spread to cover much of the grazing land in Baringo District, especially around the lake. The shrub forms an extensive and impenetrable thicket that gradually chokes out other plants, including the acacia tree and grass, leaving much of the soil bare and prone to erosion. It has deep roots, and is likely to be linked to the lowering of the water table in the areas that it colonizes (Andersson 2005).

f) Overharvesting

According to Odada *et al.*, (2006) the majority of the fishery resources in Africa are overexploited. In total, 791 freshwater species are known to be threatened by harvesting (including fishing and gathering), 775 of which are freshwater fish. Local over fishing for food is affecting to 530 of the freshwater fish assessed and 149 (6%) of the threatened taxa. As a consequence, this is considered one of the main causes of threat for freshwater fish in the region together with water pollution. In many freshwater bodies, including Lake Baringo, increased harvesting has led to changes in fish community structures and distributions, with an overall reduction in recruitment. Over fishing also causes a decline in average fish size and often lowers trophic levels of fish communities following the disappearance of larger species. It can also reduce genetic diversity, especially when the stock size is greatly reduced from natural levels. Tilapias (*Oreochromis*) are the most targeted group of freshwater fish.
2.7 Conceptual framework

The link existing between human activities, geological processes and water, sediment quality and ecological integrity of fresh water ecosystems has been clearly shown in the recent past. However, the link has been interrupted by the notable increase in the human population growth and industrial development which has exerted pressure on the fresh water bodies and consequently has led to their contamination. Surface water bodies are more exposed to this problem through the increase in anthropogenic activities, runoff, erosion and sedimentation. As metals enter the aquatic environment, either as dissolved ions or associated with particulate matter, they become associated with the sediments through precipitation reactions, adsorption to sediments, and suspended particulates and their subsequent deposition and accumulation by aquatic organisms, eventually settling as detritus biomass. Depending upon factors that control bioavailability (e.g., grain size, sulfides, etc) these heavy metals can exert a toxic impact to the infaunal benthic organisms, potentially reducing the availability of key food organisms to fish such as salmonids.

The conceptual framework (Figure 1) shows the independent, intervening and the dependent variables in this study. These variables show the link that exists between human activities, geological processes and water, sediment quality and ecological integrity of the fresh water ecosystems. Increase in the human activities and the geological processes (independent variables), leads to the inputs of pollutants (including heavy metals) in the aquatic ecosystem and this affects the life inhabiting it from the macroinvertebrates to the fish (dependent variables). This in turn leads to degradation of the ecosystem through the deterioration in water and sediment quality. The enforcement of environmental policies and regulations governing solid waste management, human settlement and industrial development (intervening variables) leads to a decrease of these activities thus enhances the quality of the ecosystem.



Figure 1: Conceptual framework showing the independent, intervening and dependent variables in this study.

2.8 Scope

This study focused on the assessment of some selected physico-chemical parameters of water, determination of sediment characteristics: particle size composition, sediment organic matter and heavy metal concentrations in water and sediments in Lake Baringo. The heavy metals studied were, copper, cadmium, mercury and lead. This study was limited to a few sites on the lake (Kampi ya Samaki, Salabani, Endao River, Molo River, and Ol kokwa) which were selected based on presumed heavy metal concentrations and the distribution as well as the levels of human and animal disturbances.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Study site description

Lake Baringo (Figure 2) is located in the Eastern arm of the Great Rift Valley (00°30' N and 00°45'N, and 36°00'E and 36°10'E), in the sparsely populated Marigat division in the semi-arid Baringo County in Kenya. It has a surface area of about 130 km² which may rise to 168 km² during the rainy seasons and an altitude of about 1100 m.a.s.l. (Odada *et al*, 2008). Some of the seasonal rivers drain into the lake, include Ol Arabel, Makutan, Tangulbei, Endao and Chemeron. Perkerra and El Molo are perennial rivers, although studies have revealed that in the dry seasons these exhibit significantly reduced water discharges. The waters are assumed to infiltrate through lake sediments into faulted volcanic bedrock. Unlike many Great Rift-Valley lakes of Kenya, it is a freshwater lake providing water to thousands of people in the area.

The lake is part of the Great Rift Valley system. To the west of the lake lies the Tugen Hills, an uplifted fault block of volcanic and metamorphic rocks whereas to the east lies the Laikipia Escarpment. The lake is fed through inflows from the Mau Hills and Tugen Hills. Studies have shown a decline in fish stocks and water levels particularly through frequent droughts and over-irrigation in the lake's drainage basin. The lake is commonly turbid with sediment, partly due to intense soil erosion in the catchment, especially on the Loboi Plain south of the lake (Lake Baringo, 2012).

The lake is habitat to hundreds of birds and animal species including the migratory flamingo species and resident species such as comorants, kingfishers, pelicans and fish eagles (Kenya Birds-Lake Baringo, 2008). The lake also provides an invaluable habitat for seven fresh water fish species of which *Oreochromis alcalicus baringoensis*, is endemic to the lake. Lake fishing is important to local social and economic development. Additionally the area is a habitat for many species of animals including the hippopotamus (*Hippopotamus amphibious*), nile crocodile (*Crocodylus niloticus*) and many other mammals, amphibians, reptiles and the invertebrate communities (Kenya Birds-Lake Baringo, 2008).

The rainfall in the lake basin is bimodal, intense, and erratic. The long rains occur in the months of April to August, whereas the short rains fall from October to November. The area experiences annual rainfall amounts of 450-900 mm (Johansson and Svensson, 2002). The geology of the area is mainly undifferentiated volcanic rocks, while the soils are of clay type. The landscape is characterized by steep slopes from the Tugen Hills and Eldama Ravine Highlands to the Perkerra River, grading in to gentle slopes, and finally to the floodplains of Marigat and Lake Baringo.

3.1.2 Sampling sites and sample collection

The research design was an ecological survey and based on the research objectives sampling sites were purposefully selected as sites receiving effluents from the watershed i.e. River El Molo mouth, Kampi Samaki wastewater discharge point, Salabani River mouth and Endao River mouth. Ol Kokwa sampling point was used as the reference site owing to its low population and fewer human activities. Global positioning System (G.P.S.) Navigational Unit (Garmin 2 model) was used to locate the sampling sites for ease of subsequent sampling. Map of Lake Baringo (Figure 2) shows the selected sampling points.



Figure. 2: Map showing water and sediment sampling sites in Lake Baringo (S1-Kampi ya Samaki discharge point; S2 Salabani discharge point; S3- Endao River discharge point, S4-Molo River discharge point and S5- Ol Kokwa point).

The table below shows the site coordinates where the replicates were collected during the sampling periods.

SAMPLE SITE	X	Y	MAJOR HUMAN ACTIVITIES
Kampi Samaki 1	169073	68324	Sedimentation, domestic and industrial
Kampi Samaki 2	169100	68354	effluents, sewage discharge.
Salabani 1	169037	65318	Deforestation, sedimentation, fertilizer
Salabani 2	169237	65105	and pesticide use, overharvesting fish
Endao River 1	170767	63707	Sedimentation, agricultural runoff,
Endao River 2	171248	63043	overharvesting fish, water extraction and
			transfer, development and dams,
			domestic and industrial effluents
Molo River 1	173275	58954	Sedimentation, agricultural runoff,
Molo River 2	173773	58585	overharvesting fish, water extraction and
			transfer, development and dams,
			deforestation, domestic and industrial
			effluents
Ol kokwa 1	174147	65948	Sedimentation, overharvesting fish.
Ol kokwa 2	173999	66310	

Table 2: GPS coordinates of sampling sites

3.2 Sediment sample collection and analysis

3.2.1 Sediment sample collection

Two replicate sediment samples were collected from each of the five sampling sites during each sampling occasion between August and February (2014) using a grab sampler. The samples were then placed and wrapped in polythene bags and kept in cooler boxes before being transported to the laboratory for analysis. Thus, a total of 20 samples of sediments (5 sites X 4 sampling occasions) were collected by the end of the study. This sampling strategy enabled us study spatial variations in heavy metal concentrations in sediments among the other variables being studied.

3.2.2 Sediment sample analysis

The samples were analyzed for total extractable metals using the multi-acid digestion method as described by Briggs and Meier (1999). A 50 mg of sediment sample was dried and digested in a matrix of ultra-pure nitric acid and Hydrogen Flouride and nitrogen peroxide and brought to a final volume of 100 ml in 2% ultra-pure nitric acid. The trace metals that were analyzed included Pb, Cd, Cu and Hg. Metal concentrations were measured by an Atomic Absorption Mass Spectrophotometer (AAS) (Analyst 800 (Producer – company PerkinElmer Inc., USA; year of produce – 2003) following American Public Health Association handbook (APHA, 1998) methodology.

Sediment organic carbon (OC) was estimated using an equation given by Ball (1964), where the Loss on Ignition (LOI) value for each sediment sample was multiplied by 0.6. This was achieved by transferring 5-g sample for the AAS metal determination and a second 5-g sub-sample transferred to an aluminum weighing dish for measurement of percent water (by drying at 105°C to constant weight and percent loss on ignition (LOI); by ramped heating to 450°C for 4 hours).

 $LOI_{450} = ((DW_{105} - DW_{450}) \div DW_{105}) \times 100$

Where

- LOI $_{450}$ is LOI at 450° C
- DW ₁₀₅ dry weight of sample before combustion and
- DW_{450} dry weight of the sample after heating at 450° (both in grams).

Sediment particle size classification was done by standard method of analysis by sieving. The dried samples of sediment were passed through a series of sieves in a shaking machine where each successive sieve being finer than the preceding one. The fraction remaining on each sieve was weighed and its weight expressed as a percentage of the weight of the original sample.

3.3 Water sampling and analysis for metals

On each sampling occasion, two replicate water samples were collected using sampling bottles on the surface from each of the five sampling sites. Thus, a total of 20 samples of sediments (5 sites X 4 sampling occasions) were collected by the end of the study for laboratory analyses. While in the field, all sample bottles were labeled before collection to avoid mix up of samples. All equipment used for sample collection, storage and analysis of heavy metals were pre-cleaned using high-purity nitric acid and rinsed with water to ensure that they are tracemetal free. After rinsing, the bottles were stored in double-bagged zip-lock polyethylene bags. Such cleaning and storage procedures ensured that there are no detectable metal contaminants in the sampling equipment (Shafer *et al.*, 1997). The water samples were collected in polypropylene bottles and acidified with ultra-pure HNO₃ to pH < 2 and stored at 4°C prior to heavy metal analyses. The bottles were immediately sealed to protect them from contamination and aeration. The samples were put in a cooler box filled with ice cubes and transported to the laboratory for analyses. Metal concentrations were determined by the atomic absorption spectroscopy with the use of an Air Acetylene Flame and Single Element Hollow Cathode Lamp.

Other water quality physico-chemical variables known to affect dissolved metals were measured (pH, air and water temperature and electric conductivity) in the field. Air and water temperature, electrical conductivity, salinity, total dissolved solids and pH were measured insitu using a multimeter probe (Hydro lab-Quanta Water Quality Monitoring System model no. QD 02233) and recorded in a field note book where two readings were recorded per variable. The hydro lab was calibrated in the laboratory before each sampling occasion to provide accurate and reliable water quality measurements.

3.4 Statistical analyses

3.4.1 Water and Sediment analysis

Values obtained were computed, analyzed and presented as mean \pm standard deviation using SPSS ver. 17. Data collected were subjected to statistical analysis. One-way analysis of variance was used to test differences, and the means differences using LSD Test. Pearson correlation was to determine correlations between physicochemical parameters. Levels of significance of differences in the values of the physicochemical parameters of the water and sediment characteristics were determined during the study periods. Differences were regarded significant at 95% confidence limit ($p \le 0.05$).

3.4.2 Heavy metal analysis

The data was tested for normality and homogeneity of variance using Kolmogorov-Smirnov Normality Test ($p \le 0.05$) and Levene's Test for equal variances ($p \le 0.05$), respectively (SPSS ver. 17). Using data that satisfy the assumptions of normality, heavy metal concentrations in water and sediment samples from the selected study sites were compared using analysis of variance (ANOVA) to test for differences among sites ($\alpha = 0.05$). Pearson correlation was used to establish inter metallic relationships. The Table below shows a summary of the statistical tools used in the analysis of the data.

Table 3: Summary of statistical analysis used to test/analyse data

<u>Test</u>	What was tested/analysed
Kolmogorov-Smirnov	Normality of data obtained for the variables under investigation
Levene's	Homogeneity of variance of the data obtained
Descriptive statistic	Individual means for various variables in each sampling site.
LSD	Mean comparison and separation individual variables
Correlation analysis	Relationship of selected water quality parameters

CHAPTER FOUR

4.0 RESULTS

4.1 Physicochemical parameters of surface water

The mean (\pm standard errors) values obtained for the physicochemical parameters are presented in Table 4.

Table 4: Means (\pm SE) of various physicochemical variables in water samples collected from Lake Baringo. *S1-Kampi Samaki; S2- Salabani; S3-Endao River; S4-Molo River and S5-Ol Kokwa Island*. Significant levels for ANOVA test are n.s = not significant, * = 0.5, ** = 0.01 and *** = 0.001, n = 5

	SITES						
Variables	S1	S2	S 3	S4	S5	ANOVA	
						F value	
Water Temp (°C).	28.0±0.1	28.2±0.2	27.7±0.4	29±0.15	29.1±0.2	1.0*	
Air Temp (°C).	37.5±0.5	40.5±0.5	36.5±0.5	42.0±0.0	43.5±0.5	43.7***	
pН	6.5±0.3	8.1±0.07	7.8±0.3	7.8 ± 0.0	8.1±0.1	21.6***	
EC (µs/cm)	371.5±0.5	377.0±1.5	371.0±0.5	370.0±0.5	372.0±0.5	1.7*	
TDS (mgl ⁻¹)	372.0±1.0	374.0±0.5	367.0±1.0	367.0±1.0	369.0±0.5	13.3**	
%Salinity	0.1±0.0	0.1±0.0	0.1±0.1	0.12±0.1	0.12±0.2	0.5ns	

The water temperature measurements during the sampling periods ranged from 27.7 °C and 29.1 °C recorded at S 3 and S 5, respectively (Table 4). The same sites also recorded the lowest and the highest air temperatures, 36.5 °C and 43.5 °C. One way ANOVA showed that spatial variations of water temperature and air temperature was statistically significant ($F_{(4, 25)} = 0.95$, p < 0.95). Post hoc tests revealed that the mean difference of water temperature at sites 1 and 3, 1 and 5, 2 and 3, 2 and 5 and 4 and 5 were statistically significant at the level of 0.05

(*LSD test,* p = 0.031, 0.018, 0.011, 0.007 and 0.031, respectively). Analysis using Pearson Correlation showed a strong relationship between air temperature and water temperature with p=0.981. The pH ranged from circumneutral to slightly alkaline with its values ranging between 6.5 (S 1) and 8.1 (S 5). One way ANOVA revealed that there was a significant difference in the pH readings between the sampling sites (F _(4, 10) = 21.5 p<0.001).

The highest mean conductivity was recorded at S 2 ($377\pm1.5 \ \mu$ Scm⁻¹) while the lowest was recorded at S 4 ($370.05\pm1.0 \ \mu$ Scm⁻¹). One way ANOVA showed that the spatial variation of conductivity was statistically significant amongst the sampling sites (F _(4, 29) = 1.72, *p*<0.5) (Table 3). Pearson correlation showed a strong relationship between EC and TDS at the level of 0.01. Percent salinity measured for the Lake were low and ranged between 0.11% and 0.13% and the lowest and highest means were recorded as 0.014±0.1 and 0.007±0.005. There was no statistically significant difference at the level of 0.05 in salinity levels between the sampling sites (*F* _(4, 9) = 0.5, *p*>0.739).

4.2 Heavy metal concentrations in water samples.

The heavy metal concentration in water from all sampling sites were recorded as follows; $Cu = 0.023\pm0.01$ mg/l, $Cd = 0.025\pm0.01$ mg/l, Hg, $= 0.002\pm0.0003$ mg/l. The concentrations of Cd were higher in all the sites followed by Cu, Hg while Pb was below the limits of detection. A one-way Analysis of Variance revealed that there was no significant differences at p = 0.05 in Cu amongst the sampling sites (F _(4, 29) = 0.23 p>0.92). The highest Cu content was recorded at S 1 and the lowest levels recorded at S 5 (Figure 3). Comparing with the recommended WHO / EPA value for Cu (50 mg/l), one sample t- test at 0.05 level showed that there was a significant difference as the mean difference value obtained was - 49.97.



Figure. 3: Spatial variation of Cu concentration in water during the study period at different sites. Vertical Bars=Means± Standard Error. S1 - Kampi Samaki; S2- Salabani; S3-Endao River; S4-Molo River and S5-Ol Kokwa Island.

Cd concentration measured in the lake water also showed some variation among the sampled sites. The highest reading was recorded at S 2 (0.028 mg/l) while S 4 had the lowest reading (0.024 mg/l) (Figure 4). One way ANOVA showed that the spatial variation of Cd was not statistically significant at $p \le 0.05$ amongst the sampling sites with F _(4, 29) = 0.024 p=1.0. Comparing with the recommended WHO / EPA value for Cd (10 mg/l), one sample t- test at 0.05 level showed that there was a significant difference as the mean difference value obtained was - 9.97.



Figure 4: Spatial variation of Cd concentration in water during the study period at different sites. Vertical Bars=Means± Standard Error. S1-Kampi Samaki; S2- Salabani; S3-Endao River; S4-Molo River and S5-Ol Kokwa Island.

Hg values were recorded to be low in all the sampling sites (Figure 5) and showed that there was no statistically significant variations amongst the sampling sites at the 0.05 level (i.e F $_{(4,29)}$ = 0.19, p=0.94). S5 recorded the highest reading followed by S4 while the lowest reading was obtained at S3. Comparing with the recommended WHO / EPA value for Hg (0.02 mg/l), one sample t- test at 0.05 level showed that there was a significant difference as the mean difference value obtained was – 0.017.



Figure 5: spatial variation of Hg. concentration in water during the study period at different sites. Vertical Bars=Means± Standard Error. S1-Kampi Samaki; S2- Salabani; S3-Endao River; S4-Molo River and S5-Ol Kokwa Island.

4.3 Heavy metal concentration in sediments

The heavy metal concentration in the sediments at all sampling sites ranged between Cu = 12.97 ± 1.0 , Cd = 1.15 ± 0.4 , Hg, = 0.25 ± 0.1 and Pb concentrations were below limits of detection.

For the values obtained for Cu in the five sampling sites, a one way ANOVA revealed a statistically significant difference between the sampling sites at $p \le 0.05$ i.e $F_{(4,14)} = 6.945$ p=0.01. However, the separation of means showed that S2 and S3, S2 and S4, S2 and S5, S3 and S5, S3 and S3 and S5 were not significantly different from each other (LSD test: p>0.05), respectively. All values of heavy metal concentrations were higher in all the sites, from the sediments samples than the water samples.



Figure 6: Spatial variation of Cu. Concentration in sediments during the study period at different sites. Vertical Bars=Means± Standard Error. S1-Kampi Samaki; S2- Salabani; S3- Endao River; S4-Molo River and S5-Ol Kokwa Island.

There was no significant differences in the levels of Cd at $p \le 0.05$ level amongst the sampling sites (F _(4, 14) =0.03, p= 1.0). Observations in Cd concentrations were similar to those of made for the Cu concentrations where the sediment samples from S2 recorded the highest reading (Fig. 7).



Figure 7: Spatial variation of Cd concentration in sediments during the study period at different sites. Vertical Bars=Means± Standard Error. S1-Kampi Samaki; S2- Salabani; S3-Endao River; S4-Molo River and S5-Ol Kokwa Island.

Concentrations of Hg from the sediments are depicted in figure 8. There were no significant spatial differences at p ≤ 0.05 in mean concentrations of Hg in all the studied sample sites (F _(4, 14) = 0.36 *p*=0.83). Further, S1 and S2 recorded a slightly lower reading in the mercury concentration. Site 3 had the highest concentration though not statistically significant.



Figure 8: Spatial variation of Hg. concentration in sediments during the study period at different sites. Vertical Bars=Means± Standard error. S1-Kampi Samaki; S2- Salabani; S3-Endao River; S4-Molo River and S5-Ol Kokwa Island.

4.4 Sediment characteristics (Grain size and TOC)

There was a significant difference in percent sand amongst sediment samples collected from all the sites at p ≤ 0.05 (F _(4, 14) = 5.2 p=0.02). Similarly percent silt and clay also showed a statistically significant difference amongst the sampling sites. The amount of sand contained in the sediment samples collected ranged from 37.9% to 84.6% and the highest readings were recorded at S1 (Table 5). The lowest reading for clay was recorded at this site. Further analysis using LSD test showed that at the level of 0.05, the mean differences of sand, silt and clay in S1 varied significantly, whereas there were no significant difference amongst the sediment particle size classes for the other sampling sites. S3 had the lowest amount of sand but recorded the highest reading for silt with an average amount of clay. S4 and S5 almost had the same amounts of silt and clay.

Table 5: TOC and grain size distribution of sediments (means ±SE) in Lake Baringo. *S1-Kampi* Samaki; S2- Salabani; S3-Endao River; S4-Molo River and S5-Ol Kokwa Island. Notes: significance levels *=0.5 and **=0.01. df =4 and n=14

	SITES						
Variables	S1	S2	S 3	S4	S5	F value	
Sand (%)	71.7±12.2	47.2±0.4	38.9±1.0	44.0 ± 0.8	46.9±0.8	5.2*	
Silt (%).	14.1±5.7	25.1±0.4	27.2±0.9	28.3±0.8	26.1±1.2	5.7**	
Clay (%).	14.1±7.2	27.7±0.7	34.0±0.8	27.8±1.1	27.0 ± 0.8	4.7**	
TOC	12.3±0.9	11.8±2.4	9.41±0.6	10.1±7.8	11.2±0.7	0.9*	

With respect to TOC, the mean values in the five sediments samples collected ranged from 9.4 % to 12.3 %. S1 recorded the highest reading of TOC. Similarly, S3 also recorded the lowest TOC and the highest amount of clay. Similarly, TOC levels in sediments were statistically significant at the $p \le 0.5$.

Further analysis using Pearson correlation test revealed that negative correlations existed between sand and all the heavy metals studied. However low, positive correlations existed between the heavy metals with silt and clay as shown in Table 6.

Table 6: Correlations between Cu, Cd and Hg concentrations and sediments of different grain
 sizes. Notes: * significant at 0.05 level.

Heavy metal	Sand	Silt	Clay
Cu	-0.57	0.56*	0.57*
Cd	-0.23	0.20	0.25
Hg	-0.42	0.30	0.48

CHAPTER FIVE

5.0 DISCUSSION

5.1 Physico-chemical Parameters.

With the increase in pollution in aquatic ecosystems especially in developing countries, understanding of pollutants and their impacts on human and environmental health is paramount. Chemical pollutants especially the persistent chemicals, with the potential of adversely impacting on the health of aquatic organisms, enter the surface waters through various pathways even at extremely low concentrations (Igbinosa *et al.*, 2012). It is thus important that the sources, concentrations and potential impacts of pollutants including heavy metals be studied so as to protect human and environmental health. In this study, baseline information on the physicochemical qualities and heavy metals concentrations in water and sediments of Lake Baringo were investigated. The marked variation and significant differences in physicochemical qualities of the water indicate different environmental conditions and variation in anthropogenic inputs. The variations in heavy metals in water and sediments may thus be attributed to patterns of water use in the watershed, pH, dissolved organic carbon, hardness (Ogendi *et al.*, 2007; Idowu *et al.*, 2013).

The water temperature observed in this study ranged from 26 to 27.7°C and varied significantly with sampling stations (p < 0.05). There was no significant correlation between temperature and other variables tested. The observed trend could be attributed to the dilution due to heavy precipitation and run-off from the catchment areas during the rainy season as was observed by Igbinosa *et al.*, (2012). The significant variations in temperature could also be attributed to the different sampling times where some stations were sampled early in the day and some stations sampled later in the day. Temperature is dependent on factors such as sun light and depth and does not undergo drastic changes during the year in lacustrine environments (Idowu *et al.*, 2013) as compared to fluviatile environments. Water temperatures were high during the sampling period probably because of the warming effects of the sun and low relative humidity which could increase evaporation of water (Omondi *et al.*, 2014). Water temperature in Lake Baringo to range between 24.9 °C to 26.2 °C and Ouma and Mwamburi (2014) measured

temperature to range between 19.7°C to 28.8°C, with a mean value of 26.5°C in Lake Baringo. Patterson and Kiplangat (1995) attributed high temperatures to dissolved and suspended matter. The water temperature range in this study for Lake Baringo therefore approximated those of related studies in this water body.

The hydrogen ion concentration (pH) of water is an important parameter as many biological activities can occur only within a narrow range and any variation beyond the permissible limits can be fatal to a particular organism. The pH was near neutral during the study period and ranged between 7.62 and 8.14 pH units and it was within the range for inland waters (pH 6.5 - 8.5), as reported by Ochieng *et al.* (2007). This is a result of the presence of carbonates and bicarbonates derived from the carbonatite volcanic rocks in the lake's drainage basin. Odour *et al.* (2003) recorded a pH range from 8.0 to 10.5, with insignificant diel variations. A recent study by Ouma and Mwamburi (2014) recorded a pH range between 7.8 and 8.5 with a mean value of 8.3. The higher pH value at the surface water may be attributed to the release of phosphorus from detergents used during cleaning / washing of clothes, utensils etc. at different reaches of the lake (Mazumdar *et al.*, 2007). Ibrahim *et al.*, 2009 reported pH range of 6.09 - 8.45 as being ideal for supporting aquatic life. Thus, the pH range obtained in this study is within the acceptable level of 6.0 to 8.5 for culturing tropical fish species and for the recommended levels for drinking water (WHO, 1993).

Electrical conductivity (EC) is an estimate of the amount of total dissolved solids (TDS) or the total amount of dissolved ions in the water. Sources of dissolved ions include soil and rocks in the watershed, wastewater from sewage treatment plants, agricultural runoff, and urban runoff from roads, different club houses located on the lake, occasional washing and cleaning of automobile and machineries from the nearby garages. This study revealed that EC values correlated with the variation of TDS. The TDS content ranged from 369 mg/l - 374 mg/l whereas the EC ranged between 366 μ S/cm and 374 μ S/cm.

The EC value showed a relationship with the TDS with p=0.08 in the surface layer given that the lake is relatively shallow. Omondi *et al.*, (2014) recorded conductivity values ranging from 556 to 601 (μ Scm⁻¹) which is higher than the values recorded during this study. The fluctuating conductivity values obtained in this study could be attributed to the nature of the

inflowing rivers (such as Molo and Endao Rivers) containing high ion loads (Kiplangat *et al.*, 1999). Also the high temperatures recorded in Lake Baringo were accompanied by high evaporation rates could also contribute to the fluctuation in conductivity values in the lake (Omondi *et al.*, 2014). The salinity levels were low and they ranged between 0 and 0.15% during the sampling period and this was associated with the closed seepage of the lake and no outlets (Ochieng *et al.*, 2007). The physicochemical parameters of Lake Baringo were within the acceptable limits by NEMA and the WHO as shown in Table 7.

Parameters	KEBS / NEMA		WHO/USEPA water	Current study
	Water quality		quality guidelines	
	guidelines			
pH (units)	6.5 - 8.5		6.5 - 8.5	7.62
TSS (mg/l)	30		NA	NA
TDS(mg/l)	1200		NA	373.6
Conductivity(µSm/cm)	NA		1000	371.5
DO(<i>mg</i> / <i>l</i>)	NA		NA	NA

Table 7: Water quality standards for various parameters by NEMA and WHO/USEPA

N A – Not Available.

Source: GoK, (2006), WHO (1983, 2004) and USEPA (2002).

5.2 Heavy Metal Levels in Water

Studies have shown that due to low pH, heavy metals may be desorbed from the sediments into water (Ebrahimpour and Mushrifah, 2008; Njogu *et. al.*, 2011). A decrease in pH will increase the competition between metals and hydrogen ions for binding sites and may dissolve metal complexes, releasing free metal ions into the water column. Further, water salinity, pH and temperature have major effect on the bioavailable concentrations of most heavy metals. Thus, the threshold levels for salinity, pH, temperature and priority heavy metals may need to be based on site-specific eco-toxicology and biological effects (Njogu *et al.*, 2011).

The current study findings indicated that Cu, Cd and Hg were present in all the water samples whereas Pb values were below the limits of detection. Cu is a vital element necessary for normal organism growth and metabolism and its uptake are regulated by physiological mechanisms according to nutritional demand. At high concentrations, copper becomes toxic to the body. Cu was present in water samples from all sites but at levels below the WHO drinking water quality guidelines of 50 ppb (WHO, 1993). The highest Cu content was found at Kampi ya samaki close to main wastewater discharge point suggesting an anthropogenic contribution and the lowest levels recorded at Endao River mouth and Ol Kokwa. This could be as a result of dilution by the water from the Endao River or removal of Cu through adsorption onto particulate matter as the river flow downstream (Njogu *et al.*, 2011).

Cd occurs naturally, and only a minor constituent of surface and groundwater. It enters aquatic systems through weathering and erosion of soils and bedrock, atmospheric deposition and fertilizers in agriculture. Much of the Cd entering fresh waters from industrial sources may be rapidly adsorbed by particulate matter, and thus sediment may be a significant sink for cadmium emitted to the aquatic environment (WHO, 1992). The data obtained showed that Salabani recorded the highest amount of Cd followed by Endao River mouth. However, the readings obtained were below the WHO drinking water quality guidelines of 10 ppb (WHO, 1993). The relatively high values encountered at Endao River mouth seem to correspond to agricultural runoff entering this lake as the rivers drain through an agricultural area where there is intensive use of pesticides and animal feeds. The high concentration of Cd in these sites could also be attributed to the high percentages of silt and clay which increased the surface area for the accumulation of heavy metals which could be released to the water over time.

The concentration of Hg in Salabani was significantly higher than those recorded at the other sampling sites. However, the levels of Hg were generally low. Nevertheless, the levels of the three heavy metals were significantly lower than the USEPA guideline values for drinking water (USEPA, 2002) which is 0.02ppb. Therefore the consumption of water from Lake Baringo is not a threat to human health. However, such low concentrations can cause long-term adverse impacts due to bioaccumulation through the continuous exposure to Hg contaminated water for drinking and cooking purposes. Similar findings were observed by Ogendi *et al.*, (2007) and Ogendi et al., (2014), where heavy metal levels posed an ecosystem but not human health risk given their significantly lower concentrations compared to the WHO and USEPA guideline values for drinking water.

The selected metals for this study may have been adsorbed on suspended particulate matter and thus their significantly low concentrations compared to those from related studies and WHO drinking water quality guidelines. Comparing our data with those of other researchers, Ochieng *et al.*, 2007, obtained higher concentrations in comparison to the results obtained in this study; Cu (1.6 mg/l), Cd (4.6 mg/l) Pb (32 mg/l). This shows that the lake was fairly concentrated with heavy metals and was attributed to the high turbulence which stirs up the water increasing the solubility of heavy metals in the water column.

5.3 Heavy metals in sediments

Metals tend to accumulate in sediments from where they may be released, moving up through the food chain. Little is known about the bioavailability of sediment associated contaminants to organisms. However, it is becoming increasingly important to understand metal accumulation within food webs, because, once these heavy metals reach man, they may produce chronic and acute ailments (Karadede- Akin and Ünlü, 2007).

The study showed variations in heavy metal contents between sites. Cu was the most predominant heavy metal in the lake sediments. Kampi ya samaki contained significantly low amounts of Cu compared to the other sampling sites. The highest concentrations of Cu were noticeable at Salabani and Ol Kokwa sampling sites. Similarly, there was high concentration of mercury at Endao River mouth. Salabani and Ol Kokwar sediments consisted of fine grain particles which act as effective collectors and carriers of dissolved metals from the water column to the sediments and thus elevated concentrations of heavy metals in sediments. The abundance of fine particles is assumed to be due to anthropogenic input associated with erosion of upstream agricultural areas and settling out of the sediments in the lake due to low water currents. Similar findings were observed by Chouba *et al.* (2007) where absence of strong water currents led to accumulation of fine sediments with high metal concentrations.

Cu concentrations in sediment samples collected from Salabani sampling site exceeded the WHO limits for sediment and thus likely to adversely impact aquatic organisms particularly the benthic community. Such elevated concentration of copper is bound to impact negatively on the macroinvertebrates and by extension their predators. Elevated metal concentrations have been shown to adversely affect fish, amphibians and macroinvertebrates in terms of reproduction, growth, abundance and diversity (Ogendi *et al.*, 2008; Mize and Deacon, 2002). Rivers Molo and Endao are considered to be a major source of heavy metals into this lake as they drain through an agricultural area where pesticides and animal feeds are used. The mean metal levels in sediments in the current study were 12.97 mg/kg which is significantly lower than those measured by Ochieng *et al.* (2007) in comparison to Rift-Valley lakes (Naivasha, Bogoria, Elementaita and Nakuru). The Lake Baringo sediments had relatively higher Cu concentrations (20.95 mg/kg) which were attributed to horticultural and livestock keeping activities in its catchment. Such elevated Cu concentrations may adversely affect sediment dwelling organisms in terms of their growth, survival and reproduction. Similarly, sediments from all the sampling sites except for Salabani (17.01 mg/kg) were below the WHO recommended guidelines for Cu for such sediments which is 16 ppb as according to Ozturk, (2009). The other heavy metals, Cd, Pb and Hg concentrations in sediments were below WHO sediment guidelines limits. Comparing this study by that of Ochieng *et al.*, 2007, the concentrations of Cd were lower (0.73 mg/kg) while those of Cu and Pb were higher (14 mg/kg and 16 mg/kg respectively) than the data we obtain.

5.4 Partitioning of heavy metals in water and sediment columns

In most aquatic ecosystems, dissolved metal concentrations in overlying waters are low due to precipitation as solids or adsorption to suspended particles and the deposition of these particles in sediments. Once the metals have been deposited in sediments, biological and chemical oxidation/reduction and precipitation/dissolution reactions result in the redox stratification of both dissolved and particulate metals with sediment depth. The oxic fraction of silty sediments usually extends to depths of 2-5 mm (Atkinson *et al.*, 2007). At greater depths the sediment becomes sub-oxic, containing mixtures of oxic solid phases (e.g. Fe- and Mn-(hydroxides) in equilibrium with reduced dissolved phases (e.g. Fe (II) and Mn (II)) (Atkinson *et al.*, 2007). Once the easily reducible Fe- and Mn-(hydroxide) phases have been depleted, bacteria reduce sulfate to sulfide, which reacts to form metal sulfide complexes whose solubility controls the fraction of metals dissolved in solution (Di Toro *et al.*, 1992).

Cu is an essential trace element that can be toxic to aquatic organisms including fish when they occur at elevated concentrations. The sources are mainly aerial deposition or surface runoff and due to its affinity for particulate matter, mainly fractions of iron, manganese oxides, and organic matter, it tends to accumulate in aquatic sediments (Sedastian *et al.*, 2007). Macroinvertebrates living in and are in contact with, bed sediments, sediments act as an important route of exposure to aquatic organisms. Adverse biological effects of Cu in the sediments include decreased benthic invertebrate diversity, reduced abundance, increased mortality, and behavioural changes (Sedastian *et al.*, 2007). The likelihood of adverse biological effects occurring in response to Cu exposure at a particular site depends on the sensitivity of individual species and endpoints examined, as well as a variety of physicochemical (e.g., pH, redox potential, and particle size), biological (e.g., feeding behaviour and uptake rates), and geochemical (e.g., organic matter, metal oxide, and sulphide) factors that affect the bioavailability of Cu (Environment Canada, 1999).

The overall mean concentration of Cu in water was 33.82% (Table 8) and this is believed to be the most readily bioavailable (Sedastian *et al.*, 2007). Cu associated with sediment fractions that exhibit cation-exchange capacity or with fractions that are easily reduced is generally more bioavailable (Environment Canada 1998) which was 90.2% in this study (see Table 8). Changes in ambient environmental conditions (e.g., sediment bioturbation, decrease in pH, and increase in redox potential) can increase the bioavailability of Cu associated with inorganic solid phases, oxides of iron and manganese, and organic matter. In contrast, Cu that is bound within the crystalline lattices of clay and some other minerals that are associated with acid-extractable or residual sediment fractions is generally considered to be the least bioavailable. (Environment Canada, 1998; Environment Canada, 1999).

Heavy	Concentrati	% of the	Concentrati	% of	Proportion of	WHO
Metal species	on in the sediments (mg/kg)	total	on in the water column	the total	sediment H/Metals in water column	guidelines in water
			(Mg/l)		(P = (xD.100)/(X - xD))	
Cu	12.97	90.2	0.023	33.82	1.44	50
Cd	1.15	8	0.025	36.76	21.1	10
Hg	0.026	1.8	0.02	29.41	6.56	0.05
TOTAL	14.38	100	0.068	100	29.1	

Table 8: Overall mean concentrations of heavy metals in the water and sediments of Lake Baringo and the WHO set limits.

In fresh water ecosystems where sediments act as a final sink, Cd is an important contaminant. It displays a complex chemistry where sorption and precipitation / dissolution are governed by complex set of environmental controls like temperature, oxygen, pH, grain size and sediment composition just like other metallic contaminants. Bioturbation interferes with its chemistry as it modifies the partitioning between solid and dissolved phase as well it changes the transfer between sediments and overlying water. A study by Soster *et al.*, (1992) demonstrated that bioturbation increases the Cd and zinc fluxes from overlying water to uncontaminted sediments which could be the same case in lake Baringo.

Hg is one of the most hazardous contaminants occurring in aquatic environments and the actual kind of chemical species present strongly determines its behaviour. Species distribution and transformation processes in natural aquatic systems are controlled by various physical, chemical and biological factors. Depending on the environmental condition, mercury species may be converted to very toxic forms (methylmercury and dimethylmercury). In natural waters Hg occurs at very low concentrations, which causes many serious problems with their accurate determination (Ram et al., 2009).

The fate and toxicity of metals in the sediments is greatly dependent on the partitioning of metals between the sediment particles and the pore waters (Calmano *et al.* 1993; Simpson 2005). Dissolved metals present in the pore waters are more bioavailable and toxic than particulate metals (Chapman *et al.* 1998). In the present study, Cd and Hg were being released from the sediments to the overlying waters 36.82 % and 29.41 % respectively (Table 8). Physical processes (e.g. water currents, anthropogenic disturbance) and the activity of benthic organisms (e.g. burrowing, irrigation) were believed to cause sediment resuspension and mixing of previously redox-stratified sediments with oxygenated overlying waters. This resuspension and mixing alters metal sediment-water partitioning and metal speciation in the dissolved phase, i.e., pore waters and overlying waters (Atkinson *et al.*, 2007). The physico-chemical changes also alter the bioavailability of metals in the pore waters and the release rate (flux) of metals from the sediments (Simpson *et al.* 2002). Studies also reveal that speciation of metals released from sediments is affected by overlying water conditions, in particular the pH, salinity, dissolved oxygen concentration and amount of suspended solids (Eggleton and Thomas, 2004) which could be attributing factors in this study.

5.5 Characteristics of sediments

5.5.1 Grain size distribution

Sediment particle sizes occurring in lakes are closely related to turbulence, wave energy, and proximity to shoreline. Increase in grain sizes of sediments generally corresponds to higher energy conditions of sediment production or transport, whereas decrease in grain sizes indicates lower energies (Cohen *et al.*, 1997).

The results obtained from the study showed that Kampi Samaki sediment samples had the highest percentage of sand with low silt and clay particles. This can be explained by the low water levels as the sampling site was near the bank and that the coarser particles were easily transported and deposited there and due to the strong hydrodynamical disturbance at low lake level the finer particles were hard to be deposited (Chen *et al.*, 2004). This resulted in larger sediment particle size. The other sampling sites had smaller percentages of silt and clay as the locations were far from the banks and the depth was relatively bigger. Hence, the coarser particles have little chance of drifting to this site due to the weak hydrodynamical forces that instead facilitate sedimentation of finer particles (Svetlana *et al.*, 2012).

Particle size influences heavy metal contents in sediments. A number of studies show that finer sediments contain more heavy metals than coarser ones (Zhu *et al.*, 2006; Jernström *et al.*, 2010; Maslennikova *et al.*, 2012; Svetlana *et al.*, 2012). The main reason is that smaller grain-size particles have a larger surface-to-volume ratio. However, some studies have indicated that coarser particles show similar or even higher heavy metal concentration than finer ones and the higher residence time and/or the presence of coarser particles are possibly responsible for higher metal content in the coarser size fractions (Singh *et al.*, 1999; Ying *et al.*, 2006). In this study, Kampi ya Samaki was the only site with high percentage of coarse particles and it recorded low amounts of copper and relatively low amounts of mercury. The other sites had a higher percentage of fine particles allowing the heavy metals to accumulate in them. Pearsons correlation revealed the negative correlations. This suggests that these metals are significantly associated with clay and silt, clay-sized constituents of the surface sediments. Results showed that municipal and domestic discharges to the river through the populated urban area contained high concentrations of heavy metals.

5.5.2 Total Organic Carbon (TOC)

TOC is often treated as an important indicator of a lake's environment and it has been widely used in determining the sediment sources of organic matter. TOC is derived from different sources and can be divided into two parts: autochthonous and allochthonous organic carbon. Production of lake plankton controls the autochthonous organic carbon while TOC sourced from outside the system is the allochthonous kind (Qian *et al.*, 1997) which originate from terrestrial plants and authigenic minerals, which are transported into the lake, and indicate environmental conditions in the catchment (Mügler *et al.*, 2010).

Generally, phytoplankton has a low total organic carbon to total nitrogen (TOC/TN) atomic ratio between 4 and 10, whereas vascular land plants have a TOC/TN ratio greater than 20. Allochthonous is controlled by climate and environment in the catchment area. For instance, more precipitation and runoff from a densely developed area with a lot of vegetation will give

rise to more allochthonous organic components in the lake sediments. Therefore, the amount of allochthonous organic carbon is a more effective proxy for climate and environment, and it can reflect the past precipitation to a certain degree (Qian *et al.*, 1997). Variations in the levels TOC in the sediments reflect changes in contribution of terrestrial organic matter. Thus, the higher the percentages of terrestrial organic matter, the higher the TOC. In addition, aquatic plants also have high TOC which could lead to complexity in the interpretation of organic matter sources for macrophyte-dominated lakes (Marchand *et al.*, 2011).

The mean TOC values in the five sediment samples collected ranged from 9.4 % to 12.3%. The TOC showed variations for the different sampling sites. The relatively lower TOC levels in the Molo River and Endao River indicated a higher contribution of autochthonous organic matter to the sediments. In Salabani and Ol Kokwa sample sites, the autochthonous organic matter probably contributed to an increasing amount of organic matter in the sediments. The obvious fluctuations were possibly ascribed to the mixed contribution of autochthonous and allochthonous organic matter. The TOC in Kampi ya Samaki was the highest since the region was a major nutrient enriched area, fed by the large amount of industrial, domestic sewage and agricultural wastewater loading with relative high TOC from the catchment. Thus, relatively higher TOC levels implied a high amount of terrestrial organic matter or aquatic plants in the lake.

Organic matter is one of the factors that influence the heavy metal distribution in sediments in that the higher organic content, the higher the metal concentrations. Areas that are rich in organic matter are also richer in heavy metals, highlighting the role of organic matter in metal accumulation in lake sediments. Taking into consideration its high specific surface area, organic matter has the ability to form complexes with heavy metals (Marchand *et al.*, 2011). The behavior of Cu in aquatic ecosystems often is influenced by its strong affinity for organic matter (Ogendi *et al.*, 2007) and clay and OC can substantially influence metal binding as well as metal extraction from sediments. Salabani and Ol Kokwa recorded the highest readings of copper and relatively high TOC.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This study provided important information on the status of the Lake Baringo limnology, the heavy metal concentrations and the characteristics of sediments. The following conclusions were therefore drawn from this study:

- Based on the findings of this study, the data on physicochemical parameters on Lake Baringo were within the maximum allowable concentrations and guidelines used by various organizations (NEMA and WHO) to evaluate drinking water quality.
- 2. The metals present in the water and sediments included copper, cadium and mercury whereas lead levels were below the limits of detection. The heavy metals could be originating from the lake's upper catchment activities and the surrounding agricultural activities. The important potential pollution sources into the lake include the agricultural practices and Mouths of River's Molo and Endao. The results obtained in this study show that the pollution of the lake by heavy metals presents an ecological rather a human health concern. Salabani sediments contained copper concentrations which exceeded the recommended levels. However, none of the measured heavy metals exceeded WHO and USEPA recommended levels in water meant for human consumption.
- 3. The sediments in the lake were dominated by sand and silt and thus accounting for the observed low metal concentrations in the sampling sites. Further, the total organic carbon in most of the sediments was predominantly allochthonous (originating from outside the system). There is therefore a strong link between the lake and the immediate terrestrial ecosystem.

6.2 Recommendations

The sampling sites considered were few and the data indicated that some parts of the lake are more polluted and therefore more extensive sampling and analysis would be necessary in order to provide more data in heavy metal speciation in these inland waters to establish the potential environmental impacts. Such information would also be necessary to determine the sources of elevated levels of trace elements analyzed as well as provide more accurate baseline data which can be used by authorities in their impact assessment and future planning of activities.

To restore the lake, the soil erosion and siltation in the catchment area needs to be addressed. Preventive measures must be taken immediately to curb the periodic increase in sedimentation in the lake. This will reduce the amount of allochthonous materials entering the lake. The problem can be curbed through afforestation programmes and reducing the number of livestock in the area. Areas surrounding the lake can also be protected by fencing and planting grasses (e.g. *Chrysopogon zizanioides, Cenchrus ciliaris, Enteropogon macrostachyus* and *Eragostis superba*) and trees that can withstand water logging and drought.

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