DETERMINATION OF CONCENTRATION OF SELECTED HEAVY METALS IN TILAPIA FISH, SEDIMENTS AND WATER FROMMBAGATHI AND RUIRU ATHI RIVER TRIBUTARIES, KENYA

BY

MWANGI JOHN MUIRURI (B.Ed Sc.)

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DECLARATIONS

Declaration by student

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

Signature……Date…….

John Muiruri Mwangi
Department of Chemistry
Kenyatta University

Declaration by supervisors

This Thesis has been submitted with our approval as University Supervisors

Signature……..……Date……

Prof. Hudson Nyambaka
Department of Chemistry
Kenyatta University

Signature……Date…….

Dr. Midred Nawiri
Department of Chemistry
Kenyatta University

DEDICATION

To my dear Mother Mariam who patiently nurtured me in all spheres of life.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS AND ABBREVIATION

AAS	Atomic Absorption Spectrometer
ANOVA	Analysis of Valiance
APHA	American Public Health Association
ATSDR	Agency for Toxic Substances and Disease Registry
DW	Dry Weight
FAO	Food and Agricultural Organization
IARC	International Agency for Research on Cancer
ICP-AES	Inductively Coupled Plasma- Atomic Emission Spectroscopy
IOSHIC	International Occupational Society and Health Information Centre
NEMA	National environmental management authority
SD	Standard Deviation
SPSS	Statistical Package for Social Sciences
TWQR	Target Water Quality Range
TF	Transfer Factor
USEPA	US Environmental Protection agency
WHO	World Health Organization

ABSTRACT

Biomagnifications of toxic heavy metals to man through aquatic life occurs via industrial, runoff, agricultural, municipal and urban waste. Heavy metals such as lead (Pb), nickel (Ni) manganese (Mn) and cadmium (Cd) have World Health Organization (WHO) limits above which they are toxic. Some of the toxic effects include; reduced growth and development, cancer, damage to the nervous system, and in extreme cases death. Athi River,the second largest river in Kenya has its source in a densely populated area which has industrial and agricultural activities like coffee plantations.Some of its tributaries flow through Ruiru town, Athi River town and Nairobi City and hence the river risks untreated discharge and runoff from the activities. Nonetheless, water from Athi River is used for small scale farming and domestic purposes, while a variety of fish in this river including tilapia and mudfish are edible which could lead to accumulation of toxic metals to mankind. These pose a threat to human life hence the need to assess levels of heavy metals in Athi River. This study aimed at determininglevels of Pb,Ni, Mn, Zn, Cd and Cr in tilapia fish gills, sediments and water from Ruiru and Mbagathi tributaries of Athi River during wet and dry seasons in 2011.Purposive sampling was done to determine 4 sampling stations for fish and 10 for sediment and water, while statistical sampling was done to get fish (N=16), sediments (N=40) and water (N=40) samples. Atomic absorption spectroscopy was used for measurement of the levels of elements. The mean concentrations (mg/kg DW) of the heavy metals in tilapia fish gills ranged as follows: Pb (1.42-4.48), Ni (0.12-1.75), Mn (81.50-158.92), Zn (28.00-76.33), Cd (0.71-1.77) and Cr (ND-0.2) . The mean concentrations (mg/kg DW) of the heavy metals in sediments ranged from: Pb (23.19-51.08), Ni (0.15-2.21), Mn (280.88-1294.01), Zn (10.98-50.79), Cd (0.05-1.81) and Cr (0.69-7.33). In water, the range of mean concentration (mg/l) of heavy metals were as follows: Pb (0.004-0.047), Ni (0.007-0.062), Mn (0.187-1.048), Zn (0.002-0.695), Cd (ND - 0.01) and Cr (ND-0.068). The levels of the heavy metals increasedform water, fish and sediments. In the wet season, Zn was found to be significantly high in the fish gills, while Pb and Mn were significantly high in the sediments ($P<0.0001$). In the dry season, Zn and Cr were found to be significantly high in the sediment ($P<0.0001$). As far as the WHO's set limits are concerned, Pb was found to be high in all samples with Mn being high in fish and water while Ni and Cd were high in fish and sediments, the results show evidence of bioaccumulation of heavy metals in the fish with alarming levels that are higher than WHO limits, therefore posing potential risk for inhabitants that depend on the river. While the findings are geared towards providing baseline data on the current pollution status of this river, constant monitoring of the levels of contamination to assess the impact of the heavy metals is deemed necessary.

CHAPTER ONE

INTRODUCTION

1.1 Background

The pollution of the aquatic environment with heavy metals has become a worldwide problem and of scientific concern because the metals are indestructible and most of them have toxic effects on organisms (MacFarlane and Burchett, 2000; Censi *et al.*, 2006; Oronsaye *et al*., 2010). Heavy metals enter rivers and lakes from a variety of sources that include the rocks and soils directly exposed to surface water, in addition to the discharge of various treated and untreated liquid wastes to the water bodies (APHA *et al.*, 2005;Alaa and Osman, 2010).

There are over ten (10) heavy metals such as cobalt (Co), lead (Pb), mercury (Hg), arsenic (As), thallium (Tl), nickel (Ni),manganese (Mn), zinc (Zn), cadmium (Cd) andchromium (Cr) that have a particular significance in ecotoxicology, since they are highly persistent (Storelli *et al*.,2005). The levels of metals such as Mn, Zn, and Cr are toxic beyond a certain limit,whereas Pb, Ni and Cd are toxic even in trace amounts (Bury *et al*., 2003;Fernandes *et al*.,2008). Toxicity is realized when these heavy metal levels are higher than the recommended limit which is different for individual elements in drinking water. These heavy metals: Pb, Ni, Mn, Zn, Cd and Cr have the following WHO recommended limits: 0.01 mg/l, 0.07 mg/l, 0.4 mg/l, 3.0 mg/l, 0.003 mg/l and 0.05 mg/l respectively for drinking water and 2.0 mg/kg in fish for Pb and Ni (WHO, 2008). Weathering of rocks, a variety of anthropogenic activities that are affected by seasons, increase the concentrations of these heavy metals (Oguzie and Izevbigie, 2009). Exposure to high levels of these heavy metals can among many effects severely damage the brain and

kidneys, cause miscarriage in pregnant women, damage the organs responsible for sperm production in men and it may ultimately cause death (Karin and Terry, 2004).

Fish have been considered as one of the most significant indicators in water systems for the estimation of metal pollution level (Rashed, 2001; Oguzie and Izevbigie, 2009). Heavy metal concentrations in aquatic ecosystems are also monitored by measuring their concentrations in sediments, water and plants, since for the normal metabolism of the aquatic life, metals are taken up from water, food or sediment (WHO, 2000; Miller *et al*., 2002; Tüzen, 2003; Canlý and Atlý, 2003;Agatha, 2010; Anim*et al*., 2010).Different parts of fish such as gills, liver, kidneys and muscles have been widely investigated for heavy metals (Nussey *et al*., 2000; Begüm *et al*.,2005; Oguzie and Izevbigie, 2009).The transfer factor of heavy metals in fish organs such as gills, liver, muscles and scales in respect to water and sediments, has been studied to give information on how these metals are transferred to fish from aquatic ecosystem (Rashed, 2001; Authman and Abbas, 2007). Sediments are important sinks for various pollutants such as pesticides and heavy metals and play a significant role in the remobilization of contaminants in aquatic systems under favourable conditions(Öztürk *el al*., 2009).

Athi River is the second longest river in Kenya after the Tana River and has a length of 390 km, draining a basin area of 70,000 km². Water from this river is used for irrigation, domestic use and for fishing. Its tributaries include Ruiru, Ngong, Nairobi, Mathare and Mbagathi (formally Namanza) rivers, with MbagathiRiver flowing through Athi River town that hosts industries such as Bamburi Portland Cement, Steel Makers Industry, Blue Triangle Cement factory as well as small scale irrigation. Ruiru River flows through Ruiru town which is surrounded by coffee

plantations, high populated area and industries,resulting in increased risk of pollutants (Kithiia, 2006).

Levels of heavy metals have been found to increase from water, fish organs to sediments and vary during wet and dry seasons (Alam *et al.*, 2003; Kithiia, 2006; Wachira, 2007). The concentrations of heavy metals have also been found to decrease down the river due to dilution effect as water volume increases (Kithiia, 2006;Kar *et al*., 2008). As a result, mankind is at risk of heavy metal poisoning through drinking the Athi River water or from the bioaccumulation of the metals in the edible fish from the river. The study assessed the concentration of selected heavy metals in MbagathiRiver through Athi river town and Ruiru River around Ruiru town in both dry and wet seasons to establish if the levels were within the recommended limit by WHO. The analysis of the metals was done using Atomic Absorption Spectroscopy technique.

1.2 Problem statement and justification

Athi River water and fish risk exposure of heavy metals from untreated agricultural, urban and industrial effluents. This may results in bio-accumulation of heavy metals in man using water and eating fish from this river since its tributaries pass through populated residential areas, towns, industrial and agricultural sites. The analysis of heavy metals that include lead, nickel, manganese, zinc, cadmium and chromium is therefore justified to provide precautionary use of the water, as well as provide a basis to sensitize government authorities such as National Environmental Management Authority (NEMA) towards management of discharge into the river.

1.3 Hypothesis

For this research, it is hypothesized that the levels of heavy metal concentrations in tributaries draining into Athi River do not differ significantly from the recommended limit by WHO in rivers (WHO, 2008).

1.4 General objective

To assess the levels of selected heavy metals in tilapia fish, sediments and water fromMbagathi and Ruiru tributaries of Athi River, Kenya.

1.4.1 Specific objectives

i. To determine levels of Pb, Ni, Mn, Zn, Cd and Cr in gills of tilapia fish from Ruiru and Mbagathi tributaries of Athi River during dry and wet seasons.
ii. To determine levels of Pb, Ni, Mn, Zn, Cd and Cr in sediment from Ruiru and Mbagathi tributaries of Athi River during dry and wet seasons.
iii. To determine levels of Pb, Ni, Mn, Zn, Cd and Cr in water from Ruiru and Mbagathi tributaries of Athi River during dry and wet seasons.

1.5 Significance and outcome

In this study the levels of selected heavy metals in tilapia fish gills, sediments and water from selected tributaries of Athi River were investigated and compared with those recommended by WHO. This was found necessary since the river flows through agricultural, industrial and residential sites and hence, the risk of heavy metal exposure and toxicity to mankind through drinking its water and eating the fish. The findings showed heavy metal levels superseded the

recommended limit by WHO. This information will be used by relevant bodies such as National Environment Management Authority (NEMA) as a base for references in fight against pollution.

1.6 Scope and limitations

Six selected heavy metals were analysed from Mbagathi and Ruiru Rivers through Ruiru town and a small section after the confluence with Nairobi River. The study was not able to analyse plants as well as all parts of fish such as muscles, kidney and liver. Although Athi River is home for both tilapia and mudfish, only tilapia fish was studied as it is the most common species in the area. Age of the sampled fish could not be established or controlled which would likely influence the concentrations of the metals to be obtained.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy metals in aquatic ecosystem and their toxicity

Heavy metals refer to any metallic chemical element that has relatively high density with specific gravity that is at least 5 times the specific gravity of water(Lars,2003). Aquatic ecosystems are receiving continuously increasing levels of heavy metals with anthropogenic sources having been identified as the major sources of heavy metal pollutants in aquatic systems (Linnikand Zubenko, 2000; Farkas, 2000; WHO, 2000). In fish, gills are considered to be the dominant site for contaminant uptake because of their anatomical and physiological properties that maximize absorption efficiency from water (Tawari-Fufeyin and Ekaye, 2007). Sediments are important sinks for various pollutants such as pesticides and herbicides while, heavy metals in surface water may exist as simple hydrated ions as well as inorganic and organic complexes (Linnila, 2000; Rashed, 2001).

Some heavy metals such as copper (Cu), zinc (Zn), iron (Fe), chromium (Cr), manganese (Mn) and nickel (Ni) though essential to human body, are toxic at elevated levels, whereas cadmium (Cd) and lead (Pb) are non-essential metals andare toxic even in trace amounts. Toxicity is highly aggravated by their non degradability and tendency to bio-accumulate to toxic levels (Tüzen, 2003).Heavy metal toxicity can result in lower energy levels and damage blood composition, lungs, liver, kidneys and other vital organs, damaged or reduced mental and central nervous functionor even cause cancer (Canlý and Atlý, 2003; Tüzen, 2003;Fernandes *et al.*, 2008). Heavy metal poisoning is more likely to result from inhalation, ingestion, skin contact

with the metals or compounds from dust, fumes or materials from workplace,or in residential settings, especially homes with lead paints or old plumbing (Mtanga and Machiwa, 2007).

2.1.1 Lead (Pb)

Lead has a density of 11.3g/cm^3 atomic number 82 and is obtained from its sulphide mineral galena, carbonate cerussite, and sulphate anglesite. The ores are frequently found in combination with other recoverable metals such as Cu, Zn and Cd.Lead exists in various oxidation states (O, I, II and IV), which are of environmental importance with oxidation +2, the form in which most Pb is bio-accumulated by aquatic organisms (Akan *et al*., 2009).Lead was placed position 2 on the Agency for Toxic Substances and Disease Registry's (ATSDR)top 20 list of most dangerous heavy metals and it accounts for most of the cases of paediatric heavy metal poisoning (ATSDR, 2002).Lead has been used in pipe making, drains and soldering materials as well as battery manufacture, plumbing, ammunition, fuel additives, paint pigments and pesticides (ATSDR, 2005).

Lead has been of particular concern due to its toxicity and ability to bioaccumulatein aquatic ecosystems, as well as persistence in the natural environment (Miller *et al*., 2002; Anim*et al*., 2010). Lead is known to accumulate in fish tissues such as bones, gills, liver, kidneys and scales, while gaseous exchange across the gills to the blood stream is reported to be the major uptake mechanism (Oguzie, 2003;Tawari-Fufeyin and Ekaye, 2007). Some effects of Pb poisoning include deficiency in cognitive function due to destruction of the central nervous system, abdominal pain and discomfort, formation of weak bones as Pb replaces calcium and causes anaemia due to reduction of enzymes concerned with synthesis of red blood cells(Lars, 2003).

Lead also leads to decreased fertility, causes cancer and other minor effects like vomiting, nausea, and headache (Lars, 2003;WHO, 2008). Exposure to high Pb levels can severely damage the brain and kidneys, cause miscarriage in pregnant women, damage the organs responsible for sperm production in men and it may ultimately cause death (ATSDR, 2002).

Since fish have ability to bioaccumulate metals for a long time, the level of metal ions at a particular time may not give accurate information on concentration at that particular time. Pb levels recorded in Ogba, Warri and Ikpoba Rivers were lower than WHO and FEPA standard limit of 2.0mg/kg for food fish which implied that the consumption of these river's fish as far as Pb contamination is concerned were safe (Oguzie, 2003;Obasohan, 2008). High concentrations in fish of over 2.0 mg/kg during dry season were attributed to the high water temperatures associated with the dry season (Obasohan, 2008). Higher temperatures can result in higher activity and ventilation rates in fish and tend to lower oxygen affinity of the blood and thus increase the rate of pollutant accumulation (Nussey*et al*., 2000; Obasohan, 2008). A higher temperature could also lead to higher metabolic rates, which could induce more feeding and in turn result in increased metal concentration, if the metals are taken up via food chain (Nussey *et al.*, 2000).

Mean levels of Pb in sediments from Tyume River, were reported to range between 0.040 ± 0.005 and 0.067 ± 0.003 mg/kg, and Pb in sediments from River Nile exhibited a wide range of variation ranging from 3.1 to 76.9 mg/kg that was higher than the permissible limit of 35 mg/kg, meaning that, Nile river was polluted and needed constant control and assessment (Awofolu*et al.,* 2005; WHO, 2008;Alaa and Osman, 2010). Elevated levels of Pb could be directly detrimental to the health of the aquatic ecosystem and indirectly to man. The sediments could be

a contributing source of these heavy metals in water, hence continual assessment was highly essential (Awofolu*et al.,* 2005). Also, Agatha (2010) recorded Pb mean levels of9.43 mg/kg from Forcados River in sediment samples that were lower than the WHO recommended limit of 35mg/kg.Decreasing concentrations of Pb metal away from pollution point has been recorded which was attributed to dilution effect as a result of runoff or rain water with a big part of heavy metals in sediments being released back to water compartment in the process of remobilization (Kar *et al*., 2008;Öztürk *el al*., 2009;Agatha, 2010).

Studies from Ikpoba River recorded Pb mean concentration of 0.035mg/l in water and also Pb mean levels of 0.1 mg/l was obtained from Nairobi river which surpassed the recommended limit of 0.01mg/l for drinking water set by WHO (WHO, 2003; Kithiia, 2006;Oguzie and Izevbigie, 2009). Oguzie and Izevbigie, (2009) reported that the level of Pb in the water though lower than <1 mg/l value recommended for portable drinking water by the Federal Ministry of Environment and the World Health Organization requires that caution be taken in the discharge of effluents without treatment into Nigeria's in-land water bodies. This was because anthropogenic sources have been implicated as the major cause of pollution in aquatic environment (Kithiia, 2006; Oguzie and Izevbigie, 2009). Kithiia, (2006) recommended use of riverine vegetation as useful in absorbing heavy metals as a means of purification.

2.1.2 Nickel (Ni)

Nickel with density of 8.9g/cm^3 readily forms alloys with iron, aluminium, zinc, molybdenum, and copper and can be dissolved in dilute acids (Reilly, 2002). The most common oxidation state of Ni is +2, but compounds of Ni^+ and Ni^{3+} are well known, and Ni^{4+} has been

demonstrated(Housecroft and Sharpe, 2008).Nickel (II) compounds are known with all common anions, that is, the sulphide, sulphate, carbonate, hydroxide, carboxylates, and halides. In its compounds, Ni has a number of chemical manufacturing uses, such as a catalyst for hydrogenation,as a cathode in many rechargeable batteries, including nickel-cadmium, nickel-iron, nickel-hydrogen, and nickel-metal hydride, and used by certain manufacturers in Li-ion batteries (Davis, 2000). About 60% of world production is used in nickel-steels (particularly stainless steel) (Obasohan, 2008).

Nickel toxicity is generally low, but elevated levels have been reported to cause sub-lethal effects (Nussey *et al.*, 2000). Among the known health-related effects of Ni are skin allergies, lung fibrosis, variable degrees of kidney and cardiovascular system poisoning and stimulation of neoplastic transformation. Nickel sulphide fume and dust is believed to be carcinogenic, and various other Ni compounds may be as well (Kasprzak *et al.,* 2003). The toxicity of Ni carbonyls is a function of both the toxicity of the metal as well as the carbonyl's ability to give off highly toxic carbon monoxide gas, being explosive in air (Nussey*et al*., 2000).

Fish are known to accumulate Ni in different tissues when exposed to elevated levels in their environment (Nussey *et al.*, 2000; Obasohan and Oronsaye, 2004). Studies of heavy metal concentration in fish from the Dhaleswari and Buriganga Rivers Bangladesh recorded mean concentrations that ranged from 9.55 to 13.35 mg/kg and from 0.09 to 0.48 mg/kg, respectively (Ahmad *et al*., 2009; Ahmed *et al*., 2009b). Other findings from Ikpoba River recorded 0.02 mg/kg mean concentration of Ni in the gills of chrysichthys nigrodigitatus in the rainy season which, did not constitute immediate hazards because they fell below the 0.4 mg/kg levels

recommended in fish and fishery products by the Food and Agricultural Organization of the United Nations(FAO/WHO, 1984; Oguzie and Izevbigie, 2009).

The sediments of Buriganga River, Bangladesh showed spatial and temporal variation of Ni that ranged from 147.06 to 258.17mg/kg. It was suggested that the Buriganga River was partly a heavy metal-polluted river and the sediments were not fully safe for human health and ecosystem (Ahmad *et al*., 2009). With the gradual development of industry, intensive use of pesticides and discharge of untreated domestic sewage may further exacerbate the situation in coming years which should otherwise be minimised (Ahmad *et al*., 2009).

The typical concentrations of Ni in unpolluted surface water are given as 5.0 $x10^{-4}$ mg/l and 0.015 to 0.020 mg/l (Salnikow and Denkhaus, 2002; Awofolu *et al*., 2005).Studies in river water have indicated various levels of Ni concentrations compared to the recommended limit of 0.07 mg/l Ni in drinking water by WHO (WHO, 2003; Awofolu *et al*., 2005; Wachira, 2007). Awofolu*et al*., (2005) obtained Ni mean levels in water that ranged from 0.201 to 1.777mg/l from Tyume River. Nickel mean levels of 0.03 mg/l from Nairobi River have been recorded (Wachira, 2007). Awofolu *et al*., (2005) suggested that possible sources of Ni in surface water included anthropogenic activities, combustion of fossil fuels, old battery wastes, components of automobiles, old coins, and many other items containing stainless steel and other Ni alloys. Elevated Ni levels detected in Tyume River, water could be a contributing source to the levels in irrigated vegetables, hence continual assessment was highly essential (Awofolu *et al*., 2005).Wachira, (2007) concluded that Nairobi River water was not unsafe for human consumption as far as Ni is concerned.

2.1.3 Manganese (Mn)

Manganese makes up about 1000 ppm (0.1%) of the Earth's crust, thus making it the 12th most abundant element (Emsley, 2001). Mn occurs principally as pyrolusite (MnO_2), psilomelane $(BaH_2O)_2Mn_5O_{10}$, and to a lesser extent as rhodochrosite ($MnCO_3$). Manganese compoundsare powerful oxidizing agents with various oxidation states (+4, and +7,) and can directly combine with boron, carbon, sulphur, silicon and phosphorous (Emsley, 2001). Among the several oxidation states, the +2 oxidation state is the most stable state and the one used in living organisms for essential functions while other states are toxic for the human body. Depending on their oxidation state, Mn ions have various colours and are used industrially as pigments while $MnO_2$is used as the cathode material in standard and alkaline disposable dry cells and batteries. As a free element, it is a metal with important industrial metal alloy uses, particularly in stainless steels and Mn phosphating used as a treatment for rust and corrosion prevention on steel(Zhang and Cheng, 2007).

Though it is a required trace mineral for all known living organisms, in larger amounts, and apparently with far greater activity by inhalation, Mn can cause a poisoning syndrome in mammals, with neurological damage which is sometimes irreversible (ATSDR, 2002). Mn-related complications also include psychiatric and motor disturbances, termed manganism which has occurred in people employed in the production and processing of Mn alloys (Nussey *et al.*, 2000). People exposed to high levels of environmental pollution by Mn suffer from cerebella dysfunctions, neurological damage as was once observed in inhabitants of Groote Eylandt off the North coast of Australia (Reilly, 2002).

Studies in fish for Mn have been recorded in fish from different rivers (Oguzie, 2003; Obasohan, 2008). Mn mean levels in fish from Ogba River ranged from 0.0 to 0.75mg/kg, and also Mn concentration of 17.37 mg/kg in fish gills from River Nile have been reported (Oguzie, 2003; Obasohan, 2008; Alaa and Osman, 2010). The high concentrations of Mn are attributed to the gills being the dominant site for contaminant uptake because of their anatomical and/or physiological properties that maximize absorption efficiency from water (Alaa and Osman, 2010).

Studies of Mn in sediments from Nairobi River recorded levels that ranged from 1598.33 to 4322.83 mg/kg (Kage, 2003). Mn concentration in sediments from River Nile ranged from 139.8 to 351.8 mg/kg (WHO, 2003; Alaa and Osman, 2010).

Various levels of Mn in river water that have fluctuated from the WHO recommended limit of 0.4 mg/l have been reported (WHO, 2003; Wachira, 2007;Alaa and Osman, 2010). Mn levels from River Nile that was within the recommended limits fluctuated between 0.033 and 0.14mg/l while higher levels of 2.5 mg/l and 0.423 mg/l were recorded from Nairobi River and River Ganga respectively (WHO, 2003;Wachira, 2007; Kar *et al.*,2008;Alaa and Osman, 2010). The higher levels than the recommended limit of 0.4 mg/l was attributed to a sudden rainfall followed by high river discharge from upstream environment, industrial effluents and municipal wastes, geology of river bed and catchment area (Wachira, 2007; Kar *et al.*,2008).Adoption of adequate measures to remove the heavy metal load from the industrial waste water and renovation of sewage treatment plants are suggested to avoid further deterioration of the river water quality (Kar *et al.*, 2008).

2.1.4 Zinc (Zn)

Zinc makes up about 75 ppm of the Earth's crust, making it the 24th most abundant element with a density of 7.14g/cm^3. Zn is normally found in association with other base metals such as Cu and Pb in ores and has a low affinity for oxygen and prefers to bond with sulphur and occurs as ores such as sphalerite (ZnS), calamite ($ZnCO_3$) and zincite (ZnO). Zn forms alloys such as brass and bronze and has been used in construction of buildings, roofing and cladding (Emsley, 2001). Other uses of Zn include making circuit boards, photocopiers, dry cell batteries and its compounds are used in chemical and pharmaceutical industries such as paints, medicines and nutritional supplements (Reilly, 2002).

The toxicity of Zn is as a result of excessive absorption which suppresses copper and iron absorption while free Zn^{2+}ion in solution is highly toxic to plants, invertebrates, and even fish (FAO/WHO, 2011).Zinc salts are intestinal irritants and can cause nausea, and abdominal pain (ATSDR, 2002). Prolonged exposure to high intakes of Zn results in copper deficiency and subsequent anaemia (Reilly, 2002). There is also a condition called the zinc shakes or "zinc chills" that can be induced by the inhalation of freshly formed Zn oxide formed during the welding of galvanizedmaterials.It has been reported that zinc is able to damage nerve receptors in the nose, which can cause anosmia and recommended that consumers should stop using zinc-based intranasal cold products and ordered their removal from store shelves (Johnson *et al*., 2007;Safty *et al*., 2008)

Various Zn mean levels from fish have been recorded from different rivers that have been lower than the 75 mg/kg recommended limit for fish and fish products. Zn mean levels of 9.67 mg/kg

from Forcados River and 1.26 to 2.38 mg/kg Zn in the fish gills from Ikpoba River for the dry and wet seasons respectively, were all within the WHO set limits of 75 mg/kg Zn in fish and fishery products and did not constitute immediate hazards (FAO, 2003; Oguzie and Izevbigie, 2009;Agatha, 2010).

River sediments have been found to have levels of Zn in a number of rivers with values that vary from the recommended limit of 123 mg/kg (Kage, 2003; WHO, 2003; Alaa and Osman, 2010; Agatha, 2010). Zinc concentrations of 91.5 to 307 mg/kghave been recorded in sediments from Nile River during the dry season. 34.61mg/kg from Forcados River's sediments and 126.33-307.00 mg/kg from Nairobi River's sediments were obtained where some did not constitute immediate hazard to aquatic fauna and human consumers (Kage, 2003; Alaa and Osman, 2010; Agatha, 2010). A concentration of 0.60 mg/kg from Nairobi River was found to be below the recommended limit of 123 mg/kg for Zn in sediment (Wachira,2007). Constant monitoring of levels of contamination to assess the impact of heavy metals in the aquatic system was, however, recommended (Wachira 2007; Agatha, 2010).

Levels of Zn in rivers flowing through industrial or mining areas can be as high as 20 mg/l while soils contaminated with Zn through the mining of zinc-containing ores, refining, or where zinc-containing sludge is used as fertilizer, can contain several grams of zinc per kilogram of dry soil (Emsley, 2001). A higher Zn mean level of 76.25 mg/l than the 3 mg/l recommended limits was recorded from Forcados River while lower mean levels of 0.085 mg/l during dry season and 0.716 mg/l during wet season from River Ganga's water and 1.0 mg/l from Nairobi River's water were recorded (WHO, 2003; Kithiia, 2006; Kar *et al.*,2008;Agatha, 2010). This level was

attributed to land use activities such as agriculture system and effluent from residential and industrial area. Downstream decrease in water pollutants was observed and was attributed to the dilution effect and self purification.Constant monitoring of the levels of contamination to assess the impact of the heavy metal in the aquatic system and use of riverine vegetation was recommended as useful in absorbing heavy metals as a means of purification (Kithiia, 2006;Agatha, 2010)

2.1.5 Cadmium (Cd)

Cadmium has oxidation state of +2 and forms a number of inorganic compounds such as sulphates, chlorides and acetates most of which are water soluble. Cd is a by-product of mining and smelting of Pb and Zn and is used in nickel-cadmium batteries and paint pigments. Cd can be found in soils under agriculture from insecticides, fungicides, sludge and commercial fertilizers. Ingestion of Cd can rapidly cause feelings of nausea, vomiting, abdominal cramp and headache, as well as diarrhoea and shock. Itai-itai disease in Japan was identified among people living in Cadmium-polluted areas where rice was irrigated. Target organs include liver, placenta, kidneys, lungs, brain and bones (Reilly, 2002).

Lower Cd mean levels than the 2.0 mg/kg Cd in fish that ranged from 0.79 -0.98 mg/kg were recorded for fish from Ikpoba River, while higher Cd mean levels of 2.16 mg/kg were recorded from Forcados River (Oronsaye *et al*., 2010; Agatha, 2010). Though the concentrations were below the recommended limit, the concentrations of Cd call for caution as cumulative effects might constitute health hazards to aquatic life including man who feeds on fish (Oronsaye *et al*., 2010). Fish from Forcados River were reported to be contaminated with Cd and could be toxic to

other aquatic fauna and poisonous to human consumers, and calls for constant monitoring of the levels of contamination in order to assess the impact of heavy metals in the aquatic system (Agatha, 2010).

Cadmium in sediment from River Nile exhibited narrow range of variation ranging from 0.4 to 0.7 mg/kg that were higher than the permissible limit of 0.6 mg/kg (WHO, 2008; Alaa and Osman, 2010). The levels of Cd obtained in sediment samples from Tyume River varied between trace and 0.005 ± 0.003 mg/kg and were within the South African Target Water Quality Range (TWQR) for both domestic and irrigation purposes (Awofolu *et al.*, 2005). In the Wadi Hanifah River's sediment samples, the mean concentration of Cd was 71.7 ppb (Abdel-Baki*et al*., 2011). Heavy metal contamination in sediment can affect the water quality and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem (Fernandes *et al*., 2007; Abdel-Baki*et al*., 2011).

Studies on Cd in various river water have recorded concentrations that are higher than the WHO recommended limit of 0.003 mg/l. Cd concentrations in water from River Nile ranged between 0.002 and 0.02 ppm while Cd mean levels of 0.02 mg/l in water from Nairobi River were all higher than the recommended limit making the water unsuitable for human consumption (Wachira, 2007; WHO, 2008**;**Alaa and Osman, 2010;). Also the mean concentrations of Cd from Tyume River water ranged from 0.030±0.002 to 0.044±0.003 mg/l that was higher than the tentative TWQR guideline of 0 to 0.005 mg/l in river water for domestic use (Awofolu *et al*., 2005). Sources such as agricultural runoff where fertilisers are used, possible release of sediment bound-metals, industrial wastes and atmospheric inflow of dust could have resulted in these

levels (Awofolu*et al*., 2005; Alaa and Osman, 2010). It was concluded that water from Tyume River was unsuitable for domestic use and could have chronic health effects on users, hence continual assessment was highly essential (Awofolu *et al*., 2005).

2.1.6 Chromium (Cr)

Chromium has density of 7.2g/cm^3 and is the 21st most abundant element in Earth's crust with an average concentration of 100 ppm (Emsley, 2001). Chromium compounds are found in the environment, due to erosion of Cr -containing rocks, animals, plants, soil and can be a liquid, solid or gas. Cr can exist in valences of +3and +6 with oxidation state in Cr (III) being stable and give series of chromic compounds, like oxides (Cr_2O_3), chlorides ($CrCl_3$) and sulphates ($Cr_2(SO_4)_3$) (Emsley, 2001; Gonzalez *et al*., 2005). Cr is used in metal alloys such as stainless steel, protective coatings of metal (electroplating), magnetic tapes, and pigments for paints, cement, paper, rubber and its soluble form is used in wood preservatives as well as additive in water to prevent corrosion in industrial and other cooling system (Hingston, 2001; WHO, 2003).

Hexavalent Cr is very toxic and mutagenic when inhaled and is a known human carcinogen. Breathing high levels of the element in this form can cause irritation to the lining of the nose and breathing problems such as asthma, cough, shortness of breath, or wheezingwhere long term exposure can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation(Dayan and Paine,2001).

Higher Cr mean levels than the recommended limit of 0.15 mg/kg have been recorded in fish from various rivers (FAO/WHO 2003; Obasohan, 2008;Abdel-Baki*et al*., 2011). In the Wadi

Hanifah River's fish samples, the average concentration of Cr was 386 mg/g while Cr levels in fish from Ogba River in Benin City, Nigeria reported a minimum Cr level of 0.01 mg/kg and the highest value of 1.16mg/kg that were higher than the recommended limit (Obasohan, 2008; Abdel-Baki*et al*., 2011).

Sediments act as the most important reservoir or sink of metals and other pollutants in the aquatic environment (Gupta *et al*., 2009). Heavy metal contamination in sediment can affect the water quality and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem (Fernandes *et al*., 2007). Increased levels of Cr in agricultural soils and thus potentially in crops, can occur through the application of sewage sludge and by atmospheric deposition of fumes produced by industry (Reilly, 2002). In the Wadi Hanifah River's sediment samples, the average concentration of Cr was 9500 µg/kg (Abdel-Baki*et al*., 2011).

Chromium has been found to vary from the recommended level of 0.05 mg/l for domestic water (WHO, 2008; Abdel-Baki *et al*., 2011). Higher Cr concentrations than the recommended limit in the Wadi Hanifah River's water samples was 6.4 ppb while Cr mean concentrations from Msimbazi River waterranged from 1.414 to 0.01 mg/l. These were from points of the rivers that receive effluents loaded with pollutants from various industries including textile, which are known to contain Cr (Mwegoha and Kihampa, 2010; Abdel-Baki *et al*., 2011). Wachira (2007) recorded Cr mean levels of 0.02 mg/l in water from Nairobi Riverwhich was not higher than 0.05mg/l recommended limit for drinking water. Thus, Nairobi river water was suitable for domestic use as far as Cr is concerned (WHO, 2003; Wachira, 2007).

2.2 Methods of analysis

2.2.1 Analysis of elements

Elements including lead, nickel, manganese, zinc, cadmium and chromium have been analysed by various methods which include flame atomic absorption spectrometry(FAAS),graphite furnace absorption spectrometry (GF-AS) and inductively coupled plasma – atomic emission spectroscopy (ICP-AES) (Aceto *et al.*, 2002; Bingol and Akcay, 2005). Atomic absorption spectrometry is commonly used for it has the advantage of being highly specific, availability and selectivity (García and Báez, 2012).

2.2.2 Atomic absorption spectroscopy

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires a standard with known analyte content to establish the relation between the measured and the analyte concentrations and relies on Beer Lambert's law (Skoog *et al*., 2005; Christian, 2005).

The sample is converted into atomic vapours by a process known as atomization. The precision and accuracy of this method depends on the atomization step and therefore a good choice of the atomization method is required. The two types of atomizers are continuous and discreet atomizers. In continuous atomizers the sample is fed into the atomizer continuously at a constant rate giving a spectral signal which is constant with time. Atomization methods that are of continuous type are flame, inductively coupled argon plasma and direct current argon plasma. With the discrete atomizers, a measured quantity of a sample is introduced as a plug of liquid or solid. The spectral signal in this case rises to a maximum and then decreases to zero. An electro

thermal atomizer is one of the discretetypes. The atoms then absorb radiations of characteristic wavelengths from an external source. The atoms of lead, nickel, manganese, zinc, cadmium and chromium, absorb radiations of wavelengths of 217.0 nm,232.0 nm, 279.5 nm, 213.9 nm 228.8nm and 357.9nm, respectively from an external source which is usually a hollow cathode lamp (Eser *et al*., 2004).

This technique has been widely employed for elemental analysis in a number of matrices such as soils, water, nuts wine and wine products (Navin*et al*., 2000; Tuzen, 2003). Figure 2.1 shows a schematic diagram for the components of AAS.The two sources of radiation are continuous source which makes use of deuterium and mercury lamps and a hollow lamp which consists of an anode made of either tungsten wire or wink and a hollow cathode made of either the element of interest or its own salt. Flame atomization method consists mainly of a fuel and oxidant. Their temperatures are determined by flow rate and ratio of oxidant and fuel while the electro thermal atomizer is basically made of carbon rods. The free atoms are vaporized from the carbon atomizer into the optical light path to a monochromator which presents a monochromatic radiation to the detector. The radiations from the monochromators are received by detectors which converts them to electrical signals. Some commonly used detectors are photocells and photo multiplier tubes.

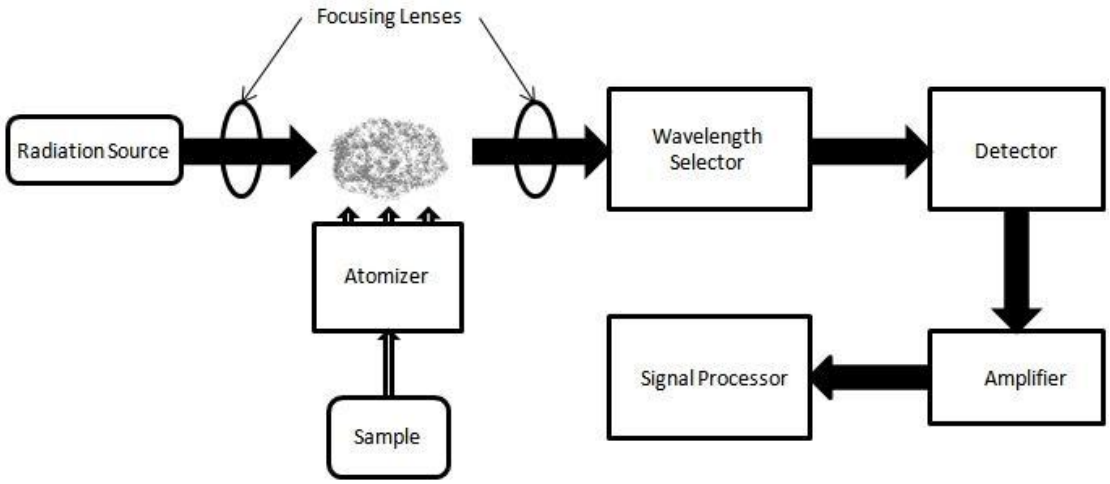

Figure 2.1: Schematic diagram of AAS equipment

a. Radiation source (Hollow cathode lamp)

This is the source of analytical light line for the element of interest and gives a constant and intense beam of that analytical line.

b. Atomiser (Flame)

The atomiser will destroy any analyte ions and break complexes to create atoms of the element of interest.

c. Wavelength selector (Monochromator)

A wavelength selector isolates analytical line photons passing through the flame and remove scattered light of the other wavelength from the flame. This only impinges a narrow line on the photomultiplier tube.

d. **Detector (Photomultiplier tube (PMT))**

It determines the intensity of the analytical line exiting the monochromator. The PMT is the most commonly used detector for AAS.

CHAPTER THREE
MATERIALS AND METHODS

3.1: Location of study sites

The study was carried out along Mbagathi and Ruiru Rivers as shown in Figure 3.1

Figure 3.2: Map of Athi River selected tributaries and the ten sampling stations

Mbagathi River originates from Ngong Hills at an altitude of 1980 metres above sea level and flows through the industries in Athi River town picking along the way industrial effluents which may contain varied heavy metals as well as agricultural and domestic effluents. Ruiru River originate from Lari Uplands and flows through coffee plantations in Kiambu county at an altitude of 2400 metres above sea level. The river flows on the left of Ruiru town where it is fed

with untreated industrial effluents such as steel mill manufacturing industries. These effluents are expected to contain such heavy metals as iron, lead, nickel and cadmium. Sampling sites were selected based on availability of fish from the two rivers and ten sampling sites for sediments and water based on sources of effluent. Along Ruiru River the upstream fishing site was located before coffee plantations while the second sampling site was located downstream of Ruiru town near the Mbagathi River confluence with Ruiru River.

For sediments and water, sampling was carried out from 5 sampling sites along Ruiru River prior to the confluence with Mbagathi River. At Mbagathi River, sampling was carried out from three sampling sites prior to the confluence with Ruiru River. After the confluence, two sampling sites were selected at about 5 kilometers from each other.

Activities along the river that prompted the purposive selection of the sampling stations are stated in Table 3.1.

Sampling station	Location	Activities
1	Before Athi River town	Fishing point and farming
2	After Athi River town	Industrial and residential activities
3	Before Ruiru Coffee plantations	Fishing point and agricultural activities
4	After Ruiru Coffee plantations and also before Ruiru town	Agricultural activities
5	Immediately after Ruiru town	To assess sewage and industrial effluent
6	After Ruiru town	Assess sewage and industrial effluent
7	Downstream of Ruiru River away from pollution points	Fishing point
8	Combined Nairobi, Mathare, Mbagathi and Ngong Rivers	Farming, industries and residential areas
9	Ruiru Rivermeets Nairobi River	Farming, industries and residential areas
10	Downstream of Athi River	Fishing point

Table 3.1: Sampling stations and the surrounding activities

3.2: Research design

Fish were sampled twice during dry (June and July, 2011) season and also twice during wet (April and May, 2011) season from four sampling stations as they were not available in other sampling stations. Sediments and water were also sampled twice during dry (June and July,2011)

and wet (April and May, 2011) seasons from 10 sampling pointsof the two selected tributaries (Ruiru and Mbagathi)of Athi River. The samples (fish and sediments) were dried until there was no further change in weight, wet digested and then analysed using atomic absorption spectroscopy for Pb, Ni, Mn, Zn, Cd and Cr.

3.3 Sampling and sample treatment

3.3.1 Fish sampling and treatment

Statistical sampling was used to obtain fish samples. A wide fishing net was pushed to the bottom of the river and dragged out. Species of tilapia fish (appendix III) were identified by its morphology. The characteristics of tilapia fish include: It has 13 – 16 dorsal spine; 10-14 dorsal soft rays; 3 anal spines; 8 – 10 anal soft ray. The upper profile of head is not convex; the lower pharyngeal boneis as long as broad, and with anterior lamella shorter than toothed area; the median pharyngeal teeth is not broadened; it has 14-16 dorsal fin and 10-14 soft rays; 8-11 lower gillrakers; It has a dark longitudinal band that appears on flanks when agitated with no bifurcated dark vertical bars on flanks. Its dorsal and caudal fins are not feebly blotched.It has brownish-olivaceous body with an iridescent blue sheen and bright green lips. It has a pinkish chest. Its caudal and anal fins are brownish-olivaceous with yellow spots, the dorsal and anal fins outlined by narrow orange band; "tilapian" large spot, extending from last spine to 4th soft ray and always bordered by yellow band. It has a yellowish or greyish caudal fin without dots, but tend to develop a greyish caudal fin with dots of increasing size during development(Teugels and Thys van den Audenaerde, 2003)

A total of 80 fish belonging to tilapia species were sampled throughout the sampling period as indicated in Table 3.2.

Table 3.2: Number of fish sampled from the four sampling stations

	Wet Season		Dry Season		
Sampling Stations	April	May	June	July	**Total**
R3	5	5	5	5	**20**
R7	5	5	5	5	**20**
M1	5	5	5	5	**20**
M10	5	5	5	5	**20**
Total	**20**	**20**	**20**	**20**	**80**

*R3- Sampling station 3 along Ruiru River. **R7- Sampling station 7 along Ruiru River. ***M1- Sampling station 1 along Mbagathi River. ****M10 - Sampling station 10 after the confluence of of Mbagathi and along Ruiru Rivers

The gills were immediately removed, packed in plastic bags and transported to the laboratory in an iced cooled box where they were stored at -20ºC. Latter the gills were dried at 105 °C in a gravity oven to constant weight. The dried fish gills for five fish from each sampling station were mixed and homogenized by grinding with a pestle and mortar into a fine powder and placed in well labeled plastic bags.

Triplicate digestions were performed following the procedure as described byTürkmen and Ciminli (Türkmen and Ciminli, 2007). Fish gills were wet digested where 1g of dried fish gills were accurately weighed using electronic balance Model AAA Adam Co limited. An18 ml of concentrated HNO_3 were first added in a Kjeldahl flask and then gently heated on hot mantle until the dense brown fumes began to appear. Hydrogen peroxide was added drop wise to clear

the brown fumes and improve the dissolving power of nitric acid. Digestion of fish gills was allowed to evaporate to about 5 ml. This was cooled and filtered (using Whatman No 42 filter paper) into 25 ml different clean and dry volumetric flask and then diluted to the mark with distilled water. The digested samples were then transferred into separate plastic bottles, labeled and stored awaiting for analysis (Türkmen and Ciminli, 2007). For background correction, six blanks were digested as pre-test samples and each of the blanks was analysed for Pb, Ni, Mn, Zn, Cd and Cr by atomic absorption spectrophotometer.

3.3.2 Sediment sampling and treatment

Two hundred samples of sediment (Table 3.2) were collected with a PVC pipe of 5 cm diameter which was pushed with pressure through the water to obtain sediment layer at a depth of approximately 15 cm.

Table 3.3: Number of sediment samples sampled from 10 sampling stations

	Wet Season		Dry Season		
Sampling Stations	April	May	June	July	**Total**
M1	5	5	5	5	**20**
M2	5	5	5	5	**20**
R3	5	5	5	5	**20**
R4	5	5	5	5	**20**
R5	5	5	5	5	**20**
R6	5	5	5	5	**20**
R7	5	5	5	5	**20**
C8	5	5	5	5	**20**
C9	5	5	5	5	**20**
C10	5	5	5	5	**20**
Total	**50**	**50**	**50**	**50**	**200**

*M- Mbagathi River.**R-Ruiru River. ***C-Confluence of Ruiru and Mbagathi Rivers.

Some pieces of stones were removed and the sediment samples were packed in polythene bags and transported to the laboratory where they were dried at 105 ºC until there was no further change in weight. Five dried sediments for each sampling station were mixed and crashed with a pestle and mortar to homogenize. The homogenized samples were sieved and packed in clean polythene bags prior to digestion and measurement of the heavy metals.

Triplicate digestions were performed following the procedure as described byTürkmen and Ciminli (Türkmen and Ciminli, 2007). Sediments were wet digested where 1g of dried sediments samples were accurately weighed using electronic balance Model AAA Adam Co limited. An18 ml of concentrated HNO_3 were first added in a Kjeldahl flask and then gently heated on hot mantle until the dense brown fumes began to appear. Hydrogen peroxide was added drop wise to clear the brown fumes and improve the dissolving power of nitric acid. Digestion of sediments was allowed to evaporate to about 5 ml. This was cooled and filtered (using Whatman No 42 filter paper) into 25 ml different clean and dry volumetric flask and then diluted to the mark with distilled water. The digested samples were then transferred into separate plastic bottles, labeled and stored awaiting for analysis (Türkmen and Ciminli, 2007). For background correction, six blanks were digested as pre-test samples and each of the blanks was analysed for Pb, Ni, Mn, Zn, Cd and Cr by atomic absorption spectrophotometer.

3.3.3 Water sampling and treatment

One litre plastic bottles were used to collect water at an interval of one foot deep and across the river and mixed thoroughly to have a homogenous sample. From the homogenously mixed water, five bottles of 500-ml water samples per sampling site were taken as in Table 3.3.

Table 3.4: Number of water samples from 10 sampling stations

Sampling Stations	Wet Season April	May	Dry Season June	July	**Total**
M1	5	5	5	5	**20**
M2	5	5	5	5	**20**
R3	5	5	5	5	**20**
R4	5	5	5	5	**20**
R5	5	5	5	5	**20**
R6	5	5	5	5	**20**
R7	5	5	5	5	**20**
C8	5	5	5	5	**20**
C9	5	5	5	5	**20**
C10	5	5	5	5	**20**
Total	**50**	**50**	**50**	**50**	**200**

*M- Mbagathi River.**R-Ruiru River. ***C-Confluence of Ruiru and Mbagathi Rivers.

Water samples were acidified to a pH of < 2 with analytical grade nitric acid while in the field and then transported to the laboratory for storage awaiting digestion.

250 ml of acidified water were measured and put in a clean conical flask and 5 ml of nitric acid added. The mixture was heated at 100 ^{o}C with the addition of few drops of hydrogen peroxide until there were no brown fumes and the volume reduced to about 5 cm^{3}. The mixture was then filtered using Whatman 0.45 μm filter paper in a 25-ml volumetric flask and topped to the labeled mark. The samples of water were digested in triplicates and then transferred into separate plastic bottles, labeled and stored awaiting for analysis. For background correction, six blanks were digested as pre-test samples and each analysed for Pb, Ni, Mn, Zn, Cd and Cr by atomic absorption spectrophotometer.

3.4 AAS operating conditions

The equipment used in this study included the analytical balance (Model AAA, Adam Co Ltd) and water distillation machine (Model WSB/4) both from United Kingdom and Varian Atomic Absorption Spectrophotometer (Model AA-10) from Australia. The operating conditions for the AAS are given in Table 3.2.

Table 3.5: The AAS operating conditions

Operating parameters	Pb	Ni	Mn	Zn	Cd	Cr
Wavelength (nm)	283.2	232.0	279.5	213.9	228.9	357.9
Slit width (nm)	1.0	0.2	0.2	1.0	0.5	0.2
Flame type					Air Acetylene	N_2O/acetylene
Oxidant flow rate (l/min)			1.5			
Sensitivity (ppm)	0.11	0.066	0.024	0.009	0.011	0.055
Detection limit (ppm)	0.02	0.008	0.003	0.002	0.0006	0.005
Lamp current (mA)	6	5			3	5
Optimum working range (ppm)	5.0-20.0	3-12	1.0-4.0		0.5 - 2.0	2.0-8.0

3.5: Stock solutions, working standards and calibration

Stock solutions of 1000 ppm for each metal were either prepared from analar grade granulated metal or salts of high purity (99.9%). Each metal or salt was first dried at 105 $^{\circ}$C, cooled in desiccators prior to weighing and transferred into 1 litre volumetric flasks.

To prepare 1000 ppm of Pb, Ni, Mn, Zn, Cd, and Cr solutions; 1.598 g of lead nitrate were dissolved in 2% (v/v) HNO_3 and diluted to volume in a l-L flask to make a standard solution of lead. 1.000 g of pure Ni, Mn, Zn and Cdgranules were each separately dissolved in a minimum

volume of pure HNO_3 and diluted to volume in a l-L volumetric flask with 2% (v/v) HNO_3 and 3.735 g of potassium chromate (K_2CrO_4) were dissolved in 2% (v/v) HNO_3 and diluted to volume in a l-L flask with distilled water to make standard solutions. The stock solutions were stored in plastic bottles and labeled appropriately.

Working standards were freshly prepared from stock solutions by serial dilution. During serial dilution of stock solutions, the final acid concentration was maintained at about 1% to keep the metal in free ionic state. Calibration curves of the elements under study were prepared by determining the absorbance of different concentrationsreported in chapter 4.

3.6: Method validation

The validity of the method was assessed by spiking of samples with standards of known concentrations and calculating percentage recoveries. The recovery tests for the elements are presented in Table 3.3.

Table3. 6: Recovery after spiking the metals

	Concentration (mg/l)		
Metal	un-spiked sample	spiked amount	spiked sample (mg/L)
Pb	0.396	0.5	0.89
Ni	0.2	2	2.14
Mn	10.5	15	25.11
Zn	1.73	3.5	5.18
Cd	0.50	5.0	5.6
Cr	0.3	5	5.16

3.7: Equations of calibration curves

Calibration curves were obtained by plotting absorbance readings against corresponding concentrations with optimized instrument conditions. Figure 3.2 shows the calibration curve for lead while other curves are presented in appendix II.

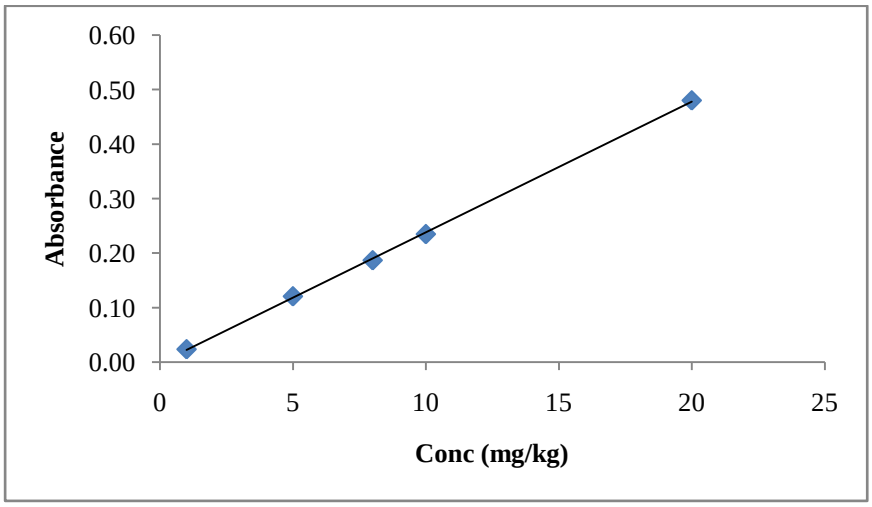

Figure 3.2: Calibration curve for lead standard.

The calibration curve gave a strong relationship (R^2= 0.999) between absorbance and concentration and therefore the instrument gave reliable results.

3.8: Recovery tests

The accuracy of the AAS analytical procedure was investigated by calculating the percentage recovery of elements. The percentage recoveries of Pb, Ni, Mn, Zn, Cd and Cr were; 98.80, 97.00, 97.40, 98.57, 102.00 and 97.20 respectively. These values were within the acceptable range of 80 to 120% expected for the elements indicating good accuracy for the analysis procedure (Duan*et al.*, 2003).

3.9: Determination and Calculation of concentration of metals

Regression equations established from a plot of absorbance readings of standards against their concentration were used to determine the concentration of Pb, Ni, Mn, Zn, Cd, and Cr in triplicates. The actual concentration of heavy metals in the samples was worked out from the obtained AAS analytical results using Equation 3.1

Actual concentration (mg/kg) = digested concentration (mg/L) x Volume digested (L)
Weight of dried sample digested(kg)**Equation 3.1**

The actual weight of Mn and Zn in tilapia fish and Pb, Mn and Zn in sediments, were obtained by multiplying the read out results with the dilution factor.

Standards of known concentrationfor Pb, Ni, and Cr in tilapia fish gills and Pb, Ni, Cd, and Cr in water samples,were added to bring the sample reading to levels within the optimum working range since their readings were below the optimum working range. The absorbance was recorded for the original sample and after the addition of the standard. Equation 3.2 was used to calculate the actual concentration of the sample (Skoog *et al*., 2005; Christian, 2005)

$$C_x = \frac{A_1 C_s V_s}{(A_2 - A_1) V_x} \quad \text{.....Equation 3.2}$$

Where;

A_1 - Absorbance of the sample before addition of standard

A_2 - Absorbance of sample after addition of standard

C_x - Concentration of sample

C_s - Concentration of the standard

V_s - Volume of standard added

V_x - Volume of sample solution

3.10:Transfer factor (TF)

The transfer factor in fish gills from the aquatic ecosystem, which include water and sediments, was calculated for the two seasons using Equation3.3 (Rashed, 2001; Authman and Abbas, 2007).

$$TF = \frac{[gills]}{[M]} \quad \text{……Equation 3.3}$$

Where:

TF = Transfer Factor

[*gills*] =concentration of metal in fish gills

[*M*] =concentration of metal in sediments or in water samples.

3.11:Data analysis

Data were analyzed with SPSS 17.0 for windows. The data were analyzed by t-test to test whether there was significance difference in the concentrations of the selected heavy metals between the dry (June and July) and wet (Wet and dry) seasons while one way analysis of variance (ANOVA)was used to test if there were significance differences in the concentrations of heavy metals between different sampling sites ($P < 0.05$).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Concentration of heavy metals in tilapia fish gills

Fishsampled from Mbagathi and Ruiru rivers in two seasons were analysed for heavy metals during wet (April and May) and dry (June and July) seasons and the results were discussed.

4.1.1 Concentration of heavy metals in tilapia fish gillsduring the dry season

Fish samples were obtained from four sampling stations,one along the Mbagathi River (station 1) and three along Ruiru tributaries of Athi River(Stations 3, 7 and 10). The mean levels of Pb, Ni, Mn, Zn, Cd and Cr in the fish gills obtained during the dry season are presented in Table 4.1.

Table 4.1: Mean concentration (mg/kg DW) of heavy metals intilapia fish gills during the dry season (Mean±Sd)

	Sampling stations				
Element	1	3	7	10	P- value
	Concentration ($\bar{x}$±Sd)				
Pb	1.71±0.08^{b}	1.42±0.05^{a}	4.48±0.05^{d}	2.10±0.05^{c}	<0.0001
Ni	0.87±0.15^{b}	0.54±0.13^{ab}	0.58±0.18^{ab}	0.12±0.06^{a}	<0.0001
Mn	81.50±17.21	132.17±42.29	132.67±44.89	124.04±44.06	0.759
Zn	49.50±0.92^{c}	35.00±0.12^{b}	37.00±1.71^{b}	28.00±4.17^{a}	<0.0001
Cd	1.52±0.10^{c}	1.23±0.06^{b}	0.71±0.15^{a}	1.77±0.12^{c}	<0.0001
Cr	0.07±0.06	0.05±0.04	0.02±0.01	0.00±0.00	0.57

*Means values followed by the same small letter within the same row are not significantly different at 95% confidence level

During the dry season, all the heavy metals under study were detected in the tilapia fish gills. The concentrations of heavy metals in the fish gills varied from one sampling station to the other with no general trend down the river.

4.1.1.1 Lead in tilapia fish gills during the dry season

The concentration of Pb in the fish gills was found in the range of 1.42-4.48 mg/kg DW. At sampling stations 7 and 10, the levels were higher than the WHO recommended limit for fish and fish products of 2.0mg/kg(WHO, 2003).These levels therefore constitute an immediate hazard to both aquatic fauna and human consumers. These stations (7 and 10) were located downstream of River Ruiru implying that the river waters had passed through agricultural, industrial and residential sites. The high levels of Pb recorded at these stations were therefore attributed to industrial and urban effluents(Kithiia, 2006; Mwegoha and Kihampa,2010). While the levels of Pb in fish sampled from stations 1 and 3 do not exceed the recommended limit, Pb poisoning from fish in these stations is still feared since even lower levels are known to be toxic (Nussey *et al.*, 2000; Obasohan and Oronsaye, 2004).In addition, long term exposure of Pb may result in slowly progressing physical, muscular and neurological degenerative processes, as well as cancer(Oguzie, 2003).

It was also found that Pb varied significantly between the sampling stations ($P<0.05$). The four sampling stations recorded significantly different concentrations with sampling stations 7 and 3 recording significantly high and low concentrations, respectivelyP(0.0001). The significantly low P(0.0001) concentration in sampling station 3 located before Ruiru town was attributed to low or no industrial and urban run-offs. Sampling station 7 located downstream of Ruiru River that

recorded significantly P(0.0001) high concentrations which could be attributed to agricultural, industrial and residential effluent(Kithiia, 2006; Obasoham, 2008; Kar *et al*., 2008; Mwegoha and Kihampa,2010).

The concentration of Pb in fish gills found in this study didn't agree with concentrations reported previously during the dry seasons in river waters. Concentrations of 0.2mg/kg and 0.33mg/kg reported in fish gills from Ikpoba and Forcados rivers, respectively did not constitute immediate hazard to aquatic fauna and human consumers, (Oguzie, 2003; Oguzie and Izevbigie, 2009; Agatha, 2010). The difference in concentration could have resulted from untreated sewerage, industrial effluent and difference in geologicalfeatures (Kar *et al*., 2008).

4.1.1.2 Nickel (Ni) in tilapia fish gillsduring the dry season

The nickel concentration from analysing the fish gills are recorded in Table 4.1.Nickel concentrations in fish were found to range from 0.12-0.87 mg/kg DW in the dry season. Except in sampling station 10, all the other sampling stations had Ni concentration that was higher than 0.4mg/kg the WHO recommended limit for Ni in fish and fish products (FAO/WHO, 2003).Fish are known to accumulate Ni in different tissues when exposed to elevated levels in their environment (Nussey *et al.*, 2000; Obasohan and Oronsaye, 2004). These high levels of Ni could have been as a result of waste from Ruiruand Athi river towns, as municipal wastes from towns have been reported to contain high levels of Ni (Oguzie, 2003; Obasohan, 2008). Based on these results, consumption of fish from these tributaries risks contracting the Ni related illness where nickel sulphide fume and dust is believed to be carcinogenicwith industrial Nicausing cancer of the respiratory tract and dermatitis (Reilly, 2002; Kasprzak *et al.*, 2003).

It was also found that Ni varied significantly between and within the sampling stations (P<0.05), with sampling stations 1 and 10 recording significantly high and low concentrations, respectivelyP(0.0001). The significantly low P(0.0001) concentration in sampling station 10 located downstream could be attributed to dilution effect as other tributaries join the main river as well as absorption by plants and sediments. Sampling station 1 located around Athi River town, recorded significantly high concentrations P(0.0001) which could be attributed to the industrial and residential effluent (Kithiia, 2006; Mwegoha and Kihampa,2010).

Higher Ni concentrations than the current study have been reported from other rivers. Concentrations of Ni that rangedbetween 9.55 and 13.35 mg/kg and between 0**.**09 and 0.48 mg/kg were recorded from Dhaleswari and Buriganga Rivers respectively (Ashraf, 2006; Ahmed *et al*., 2009b). These concentrations were above the WHO recommended limit which, constitute immediate health hazard to the people consuming fish and water. Based on Ni concentrations,it was recommended that control and monitoring of the heavy metal was necessary.

4.1.1.3 Manganese (Mn) in tilapia fish gillsduring the dry season

The results from analysing the fish gills are recorded in Table 4.1.The concentration of Mn was found to range from 81.50-132.67 mg/kg DW. In all the sampling stations the concentration was found to exceed 2.50 mg/kg, the WHO recommended limit for Mn in fish and fish products indicating that, the fish are not fit for human consumption with respect to Mn (FAO/WHO, 1984). The source of this pollution could have resulted from discharge of industrial effluents and municipal wastes, geology of river bed and catchment area (Obasoham, 2008; Kar *et al*., 2008). Manganese can lead to a variety of psychiatric and motor disturbances, termed manganism which

has occurred in people employed in the production and processing of manganese alloys (Nussey *et al.*, 2000). Adoption of adequate measures to remove the heavy metal load from the industrial waste water and renovation of sewage treatment plants are suggested to avoid further deterioration of the aquatic ecosystem quality (Kar *et al*., 2008).

Lower concentration of Mn than the current study but also higher than the recommended limit has been recorded in fish gills from River Nile (Alaa and Osman, 2010). The recorded Mn concentration of 17.37 mg/kg in fish gills could be attributed to the gills being the dominant site for contaminant uptake because of their anatomical and/or physiological properties that maximize absorption efficiency from water.

4.1.1.4 Zinc (Zn) in tilapia fish gillsduring the dry season

Mean concentrations of Zn recorded after analysing tilapia fish gills' samples are listed in Table 4.1**.** The concentration of Zn in fish was found to range from 28.00-49.50 mg/kg DW in the dry season.These results were below the 75 mg/kg recommended limit for Zn in fish and fish products, implying that the fish do not pose immediate hazard to people consuming the fish found in this area. The sampling stations, however, recorded significantly different concentrations with sampling station 1(49.50 mg/kg) recording the highest concentration and sampling station 10 (28.00 mg/kg) with the lowest concentration ($P<0.0001$). The high concentration in sampling station 1 could be attributed to industrial and/or residential effluent (FAO/WHO, 2011). The significantly low($P<0.0001$) concentration in sampling station 10 located downstream could be attributed to decrease in concentration down the river due to dilution and uptake by plants and sediments (Kithiia, 2006).

Lower concentration than the current study and also lower than the 75 mg/kg recommended limit for Zn in fish and fish productshas been reported (Oguzie and Izevbigie, 2009). A concentration of 1.26 mg/kg in the fish gills from Ikpoba River for the dry seasons did not constitute immediate hazards because it fell below the level recommended in fish and fishery products by the Food and Agricultural Organization of the United Nations (FAO, 2003; Oguzie and Izevbigie, 2009).

4.1.1.5 Cadmium (Cd) in tilapia fish gillsduring the dry season

The concentration of Cd was found to range from 0.71-1.77 mg/kg DW.The study recorded concentrations that were below the WHO's recommended limit of 2.0mg/kg for fish and fish products (FAO/WHO, 1984).However, the consumption of fish should be cautious as cumulative effects might constitute health hazards to aquatic life and man who feeds on fish (Oronsaye *et al*., 2010).Ingestion of Cd can rapidly cause feelings of nausea, vomiting, abdominal cramp and headache, as well as diarrhoea and shock. Itai-itai disease in Japan was identified among people living in Cd polluted areas where rice was irrigated and the target organs include liver, placenta, kidneys, lungs, brain and bones (Reilly, 2002).

All the sampling stations recorded values that were significantly different ($P<0.0001$), withsampling stations 10 (1.77 mg/kg) and 7 (0.71 mg/kg) recording significantly high and low levels, respectively $P<0.0001$. The presence of Cd in the fish gills from all sampling stations could be attributed to discharge of industrial effluents and municipal wastes, geology of river bed and catchment area (Obasohan, 2008; Kar *et al*., 2008).

Comparable Cd mean levels of 0.79 -0.98 μg/g in fish gills with the current study was recorded for fish from Ikpoba River, which was also below the recommended limit of zinc in fish and fish products (Oronsaye *et al*., 2010). These concentrations were also lower than the recommended limit and therefore did not pose immediate health risk to people using the water and feed on fish from the river. Based on this study it was recommended that regulatory agencies and other concerned parties to further monitor the river water which is a source of drinking water for the inhabitants down the river. The study therefore, recommends that monitoring the river which is a source of water for drinking and irrigation for the inhabitants along the big Athi River be regular.

4.1.1.6 Chromium (Cr) in tilapia fish gills during the dry season

The mean levels of Cr for all considered sampling stations are recorded in Table 4.1. The four sampling stations recorded Cr mean levels that ranged from 0.001 to 0.07 mg/kg. The concentrations recorded were lower than the recommended limit of 0.15 mg/kg for chromium in fish and fish products (WHO, 2008). This means that consumption of fish from the selected Athi River tributaries do not pose immediate threat to the population consuming fish as far as Cr concentration is concerned.However, heavy metals are known to bioaccumulate in aquatic life and therefore need constant assessment.

Higher concentrations than those reported by the current study have been reported in various rivers (Oguzie and Izevbigie, 2009).A 1.38mg/kg Cr mean levels in fish gills have been reported from Ikpoba River Nigeria during the dry season. In this study, it was reported that the levels recorded in fish gills did not constitute immediate hazards because the values fell below the recommended limit in fish and fishery products by the Food and Agricultural Organization of the

United Nations (FAO, 2003). Monitoring the levels of Cr, was however, recommended as Cr bioaccumulates in fish organs. Toxicity levels varies with hexavalent Cr being known to be very toxic and mutagenic when inhaled and also a human carcinogen with long term exposure causing damage to liver, kidney, circulatory and nerve tissues, as well as skin irritation (Dayan and Paine, 2001).

4.1.2 Concentration of heavy metals in tilapia fish gills during the wet season

The results of the four sampling stations 1, 10, 3 and 7 are recorded in Table 4.2.

Table 4.2: Mean concentration (mg/kg DW) of heavy metals in tilapia fish gills during the wet season(Mean±Sd)

	Sampling stations				
Element	1	3	7	10	P- value
	Concentration ($\bar{x}$±Sd)				
Pb	1.73±0.05	2.21±0.10	3.31±0.85	1.94±0.04	0.073
Ni	0.67±0.11^{a}	1.75±0.62^{ab}	0.29±0.06^{a}	0.83±0.23^{ab}	0.039
Mn	148.71±0.99^{a}	158.92±1.88^{c}	149.13±2.26^{b}	107.96±1.32^{b}	<0.0001
Zn	48.79±5.28^{a}	76.33±8.53^{c}	53.96±3.82^{c}	69.17±0.20^{bc}	0.005
Cd	1.29±0.19	1.44±0.12	0.96±0.23	1.60±0.12	0.081
Cr	0.02±0.00	0.02±0.01	0.02±0.01	0.02±0.00	0.873

*Means values followed by the same small letter within the same row are not significantly different at 95% confidence level

Fish gills contained all the metals during the wet season with Mn ranging from 107.96-158.92 mg/kg while Zn mean concentrations ranged from 48.79-76.33 mg/kg. Nickel, Mn and

Znanalysed from tilapia fish gills during the wet season were found to differ significantly between the sampling stations. The presence of these heavy metals in the fish gills was attributed to discharge of industrial effluents and municipal wastes, geology of river bed and catchment area (Obasohan, 2008; Kar *et al*., 2008).

4.1.2.1 Lead (Pb) in tilapia fish gills during the wet season

The concentration of Pb in fish gills was found to be in the rangeof 1.73-3.31 mg/kg DW. At sampling stations 3 and 7, the concentration was found to be higher than the recommended limit of 2.0 mg/kg in fish and fish products (FAO, 2003). As the stations are located downstream of Ruiru River, the high concentrations could be attributed to discharge from industrial, farming and residential waste. While fish have been reported to bioaccumulate Pb with time, the exposure to high Pb levels can severely damage the brain, kidneys, cause miscarriage in pregnant women, damage the organs responsible for sperm production in men, and may ultimately cause death (ATSDR, 2002). However, the concentrations in all the sampling stations did not differ significantly (P=0.073) between the sampling stations.

Lower Pb mean concentration than the current study in gills from Ikpoba River during the wet season was reported to be 0.01 mg/kg, where as Pb mean values from Ogba River ranged from 0.0 to 0.75 mg/kg (Obasohan, 2008; Oguzie and Izevbigie, 2009). These findings did not suggest immediate hazard since concentrations did not exceeded the 2.0 mg/kg Pb recommended limits in fish and fish products(FAO, 2003; Obasohan, 2008; Oguzie and Izevbigie, 2009). However, indestructibility and tendency to bioaccumulate with toxicity effect calls for constant assessment of Pb concentrations.

4.1.2.2 Nickel (Ni) in tilapia fish gillsduring the wet season

Nickel mean concentrations in fish gills are recorded in Table 4.2.The concentrationsof Ni were found to range from 0.29-1.75 mg/kg DW. In 3 out of the four sampling stations, Ni was found to be higher than 0.4mg/kg, the WHO recommended limit for fish and fish products (FAO, 2003). While only the levels of Ni in fish gills from station 7 did not exceed the recommended limit, Ni is known to be toxic and bioaccumulatesin fish (Nussey *et al.*, 2000; FAO, 2003; Obasohan and Oronsaye, 2004). These high concentrations pose nickel's toxic effects such as lung fibrosis, variable degrees of kidney and cardiovascular system poisoning, stimulation of neoplastic transformation, cancer of the respiratory tract, dermatitis and even death (Nussey *et al.*, 2000; Reilly, 2002). Agricultural runoff, industrial effluent and urban waste were attributed to these elevated levels (Kithiia, 2006; Mwegoha and Kihampa,2010).

It was also found that Ni concentrations varied significantly between the sampling stations ($P<0.05$). Sampling stations 3 and 7 recorded significantly high and low concentration respectively,P(0.0001). The significantly lowconcentration P(0.0001)in sampling station 7 located downstream of Ruiru river could be attributed to decreasing concentrations of heavy metals due to dilution effect and self purification (Kithiia, 2006). Sampling station 3 located before Ruiru town recorded significantly high concentrations P(0.0001) which, could be attributed to agricultural, and residential effluent (Kithiia, 2006; Mwegoha and Kihampa,2010).
Other studies on fish from rivers have recorded Ni mean levels that compare with that of the current study (Oguzie and Izevbigie, 2009; Agatha, 2010). Ni mean levels of 7.67and0.02 mg/kg from Forcados andIkpoba did constitute immediate hazards because they fell above the 2.0

mg/kg Ni in fish and fish products by the Food and Agricultural Organization of the United Nations (FAO, 2003; Agatha, 2010).

4.1.2.3 Zinc (Zn) in tilapia fish gills during the wet season

The concentration of Zn from analyzing the fish gills are recorded in Table 4.2. All the sampling stations recorded Zn mean levels that were below the 75 mg/kg recommended limit for Zn in fish and fish products except sampling station 3 with Zn mean level of 76.33 mg/kg DW. Sampling station 3 near the coffee plantation and agricultural farms could have contained zinc from pesticides,fertilizers, herbicide or fungicides (FAO/WHO, 2011). The exposure to high Zn levels could result to intestinal irritants, nausea, and abdominal pain while prolonged exposure to high intakes of zinc could also result in copper deficiency and subsequent anaemia (Reilly, 2002).

It was also found that Zn varied significantly between and within the sampling stations ($P<0.05$). The four sampling stations recorded significantly different concentrations with sampling station 3 and 1 recording significantly high and low concentration, respectivelyP(0.0001). The significantly low P(0.0001) concentration in sampling station 1could be attributed to low concentrations in water during the wet season (Mwegoha and Kihampa,2010).

Lower concentrations than the current study have been reported from a number of rivers (Oguzie and Izevbigie, 2009; Agatha, 2010). In these reports, Zn mean concentrations of 9.67 and 2.38 mg/kg in fish from Forcados and Ikpoba Rivers respectively, have been recorded.These levels were within the WHO recommended limit of 75 mg/kg and therefore did not constitute immediate hazard to human (FAO, 2003; Oguzie and Izevbigie, 2009; Agatha, 2010). Based on

the recorded concentrations, it was recommended that safety measures are taken to control the discharge of effluent to the river for this particular element.

4.1.2.4 Manganese (Mn) in tilapia fish gills during the wet season

The concentrationsafter analysing fish gills for Mn are recorded in Table 4.2.The concentrations of Mn in fish gills during wet season were found to range from 107.96-158.92 mg/kg DW. This indicated that all the sampling stations recorded mean concentrations that were above the recommended limit of 2.5 mg/kg of Mn in fish and fish products. It therefore meant that, fish from Athi River selected tributaries are contaminated with Mn and not fit for human consumption as far as Mn is concerned(FAO/WHO, 1984).The higher concentrations posed a health riskto aquatic life including man who feeds on fish as they cause delayed embryo development, tissue damage and reduced growth (Oronsaye *et al*., 2010).The source of these high concentrations could be industrial and municipal waste and also from geology of river bed and catchment area whose rock could be having Mn compounds that could also dissolve in water and transferred to fish (Obasohan, 2008; Kar *et al*., 2008). It is therefore suggested that the source of Mn be located and quick measures be taken to control the Mn poisoning through fish to people consuming this fish.

It was also found that Mn varied significantly between the sampling stations ($P<0.05$). The four sampling stations recorded significantly different concentrations with sampling stations 7 and 3 recording significantly high and low concentration, respectivelyP(0.0001). Sampling station 3 was located before Ruiru town and therefore recorded significantly low concentration P(0.0001). Sampling station 7 located downstream of Ruiru River recorded significantly P(0.0001) high

concentrations which could be attributed to agricultural, industrial and residential effluent (Kithiia, 2006; Mwegoha and Kihampa,2010).

Manganese mean concentrations that were lower than the current study as well as lower than the recommended limit of 2.5 mg/kg Mn in fish and fish products have been reported (Oronsaye *et al*., 2010).This study recorded Mn mean concentrations of 0.38-1.34 mg/kg from Ikpoba River which was attributed to industrial effluent and cautioned that cumulative effects might constitute health hazards to aquatic life including man who feeds on fish. This is because at higher concentrations, delayed embryo development, tissue damage, reduced growth and death of fish are caursed (Oronsaye *et al*., 2010).

4.1.2.5 Cadmium (Cd) in tilapia fish gillsduring the wet season

The mean levels of Cd analysis of the gills are recorded in Table 4.2. The cadmium mean levels recorded for all sampling stations ranged from 0.96 to 1.60mg/kg. The four sampling stations recorded Cd mean levels that were below the recommended limit of 2.0mg/kg for fish and fish products implying that Cd mean levels recorded during the wet season do not have immediate threat to man (WHO, 2003). However, due to accumulation, the levels are likely to reach toxic levels and these calls for constant monitoring. It was also found that Cd concentrations in all the four sampling stations were statistically similar P=0.081.

Cadmium concentrations that are above the current study have been reported (Agatha, 2010). This study recorded Cd mean levels of 2.16mg/kg in fish from Forcados River, which exceeded the WHO maximum permissible limit of 2.0 mg/kg for fish and fish products. The study further

reported that these concentrations were toxic to aquatic fauna and poisonous to human consumers.From the same study, constant monitoring of levels of contamination to assess the impact of heavy metals in the aquatic systemwas recommended (Agatha, 2010).

4.1.2.6 Chromium (Cr) in tilapia fish gills during the wet season

The mean levels of Cr for all considered sampling stations are recorded in Table 4.2. All the sampling stations recorded lower Cr mean levels than the recommended limit of 0.15 mg/kg for Cr in fish and fish products (FAO/WHO, 1984). The consumption of fish from the selected Athi River tributaries therefore, did not indicate immediate health hazard as far as Cr concentration is concerned for the wet season.The four sampling stations recorded similar Cr concentrations of 0.02 mg/kg in all sampling stations during the wet season which were not significantly different since P=0.873.

Chromium concentration that was above the current study has been reported (Oguzie and Izevbigie, 2009). This study recorded 1.10mg/kg Cr mean concentration in the gills from Ikpoba river Nigeria during the wet season which did constitute immediate hazards because the values fell above the 0.14 mg/kg levels recommended in fish and fishery products by the Food and Agricultural Organization of the United Nations (FAO, 2003).Hexavalent Cr is very toxic and mutagenic when inhaled and is a known human carcinogen, and exposure can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation(Dayan and Paine,2001). Based on the data obtained, stringent measures to control discharge of untreated waste were suggested.

4.2Concentration of heavy metals in sediments

Sediments sampled from Mbagathi and Ruiru Rivers in two seasons were analysed for heavy metals during wet (April and May) and dry (June and July) seasons and the results were discussed**.**

4.2.1 Concentration of heavy metals in sediments during the dry season

Sediment samples were obtained from 10 sampling stations with sampling stations 1, 2 and 8 along Mbagathi and sampling stations 3, 4, 5, 6 and 7 along Ruiru River while 9 and 10 are located after the confluence of the two Athi rivers tributaries. The mean levels of Pb, Ni, Mn, Zn, Cd and Cr in the sediments obtained in the dry season are reported in Table 4.3**.**

Table 4.3: Mean concentrations (mg/kg DW) of heavy metals in sediment during the dry season (Mean±Sd)

	Sampling stations										
	1	2	3	4	5	6	7	8	9	10	P-value
	Concentration ($\bar{x}$±Sd)										
Pb	27.17±0.19^{de}	26.37±0.34^{cd}	30.19±0.06^{f}	29.42±0.24^{f}	27.37±0.18^{de}	28.12±0.44^{e}	25.21±0.1^{b}	25.29±0.15^{b}	25.96±0.09^{bc}	23.19±0.43^{a}	<0.0001
Ni	0.92±0.16^{b}	1.12±0.14^{b}	0.61±0.11^{ab}	0.61±0.17^{ab}	1.04±0.16^{b}	0.25±0.08^{a}	0.58±0.15^{ab}	0.15±0.05^{a}	0.75±0.23^{Aab}	0.94±0.08^{b}	<0.0001
Mn	966.06±176.21^{bc}	431.71±13.76^{ab}	945.40±202.17^{bc}	1082.75±42.70^{c}	992.29±42.35^{c}	954.00±70.71^{bc}	655.88±2.64^{abc}	682.75±56.93^{abc}	684.00±27.18^{abc}	349.31±19.80^{a}	<0.0001
Zn	24.50±0.34^{ab}	24.71±0.88^{ab}	46.83±1.53^{e}	46.98±0.88^{e}	29.08±0.43^{b}	34.96±0.06^{c}	34.87±3.38^{c}	26.83±1.65^{b}	39.79±0.33^{d}	20.73±0.39^{a}	<0.0001
Cd	0.56±0.11^{ab}	0.73±0.07^{abc}	1.29±0.25^{bc}	0.92±0.28^{abc}	0.56±0.25^{ab}	1.50±0.40^{c}	0.18±0.16^{a}	0.11±0.03^{a}	0.24±0.09^{a}	0.05±0.02^{a}	<0.0001
Cr	0.69±0.21^{a}	0.73±0.23^{a}	2.54±0.04^{b}	5.46±0.34^{c}	7.33±0.44^{d}	4.92±0.27^{c}	2.71±0.77^{b}	4.21±0.32^{c}	4.79±0.64^{c}	2.67±0.27^{b}	<0.0001

*Means values followed by the same small letter within the same row are not significantly different at 95% confidence level

All the metals analysed were detected from sediments during the dry season. The presence of these heavy metals in the sediments could be attributed to discharge of industrial effluents and municipal wastes, geology of river bed and catchment area (Obasohan, 2008; Kar *et al*., 2008).

4.2.1.1 Lead (Pb) in sediments during the dry season

The Pb mean concentrations recorded in the sediments from the two selected Athi river tributaries during dry season ranged from 23.19 to 30.19 mg/kg. While these Pb concentrations were below the recommended limits of 35 mg/kg by WHO, the metal is toxic even at low levelsas it is non degradable and has a tendency to bioaccumulate to toxic levels (Tüzen, 2003; WHO, 2008).Some of the effects of Pb poisoning include deficiency in cognitive function due to destruction of the central nervous system, abdominal pain and discomfort, formation of weak bones as Pb replaces calcium and causes anaemia due to reduction of enzymes concerned with synthesis of red blood cells(Lars, 2003;WHO, 2008)The sampling stations recorded values that were significantly different where sampling` station 3 (30.19 mg/kg) recordedsignificantly high concentration while sampling station 10 recorded significantly low concentration P (0.0001). The significantly low concentration P(0.0001)in sampling station 10 located downstream could be attributed to remobilization back to water and dilution effect (Kar *et al*., 2008). Sampling station 3 located upstream of Ruiru River that recorded significantly high concentrations P(0.0001) could be attributed to agricultural, residential effluent and waste from car wash (Kithiia, 2006; Mwegoha and Kihampa,2010).Lead mean levels however, decreased downstream which could be attributed to a big part of heavy metals in sediments being released back to water compartment in the process of remobilization (Kar *et al*., 2008).

Lead mean levels of9.43 mg/kg recorded from Forcados were lower than those from obtained in the current study and also lower than the 35mg/kg recommended limit for Pb in sediment (WHO, 2003; Agatha, 2010). These concentrations were different from the current present study's results because of different geographical regions with different anthropogenic activities.

4.2.1.2 Nickel (Ni) in sediments during the dry season

The mean levels of Ni for all considered sampling stations are recorded in Table 4.3. Nickel mean concentrations recorded during dry season ranged between 0.15-1.12mg/kg DW. All the sampling stations recorded significantly different Nickel concentrations with sampling station 2 recording significantly high concentrations of 1.12 mg/kg $P<0.0001$. Sampling station 2 is situated after Mbagathi River traverses Athi River town and industrial and residential wastes could have contributed to high levels. The significantly lowconcentration P (0.0001) in sampling station 8 located downstream couldbe attributed to remobilisation of the metal back to water and plants uptake (Öztürk *el al*., 2009).Nickel metal from river sediments could be a contributing source to the levels in irrigated vegetables which require constant monitoring as elevated levels have been reported to cause sub-lethal effects (Nussey *et al.*, 2000).

Higher Ni mean concentrationsthan the current study from Buriganga River sediment ranged from 147.06 to 258.17 mg/kgwhich could be attributed to discharge of huge tannery waste and less rain water as the main reasons for the high Ni concentrations. Sediment is the ultimate depository of many chemical compounds including heavy metals from natural and anthropogenic sources. Other possible sources of Ni in the surface water that lead to the metal accumulating in the sediments include combustion of fossil fuels, old battery wastes, components of automobiles,

old coins, and many other items containing stainless steel and other Ni alloys (Ahmad *et al*., 2009).

4.2.1.3 Manganese (Mn) in sediment during the dry season

The mean concentrations of Mnin sediments during the dry season are recorded in Table 4.3. The concentration of Mn was found to range from 349.31-1082.75 mg/kg DW. Though the limit of Mn in sediments is not documented, in larger amounts, and apparently with far greater activity by inhalation, Mn can cause a poisoning syndrome in mammals, with neurological damage which is sometimes irreversible (ATSDR, 2002). Victims of Mn poisoning suffer from cerebella dysfunctions as well as awkward high-stepping gait (Reilly, 2002)**.**

It was also found that, all the sampling stations recorded mean concentrations that were significantly different$P<0.0001$, with sampling station 4 (1082.75 mg/kg) recording significantly high levels $P<0.0001$. Sampling station 4 is past the coffee plantations with high Mn concentrationsthat could be attributed to pollution emanating from extensive coffee plantations and geology of river bed and catchment area (Kar *et al.,* 2008; Alaa and Osman, 2010)**.** Sampling station 10 located downstream of Ruiru River that recorded significantly low concentrations P(0.0001) which could be attributed toa big part of heavy metals in sediments being released back to water compartment in the process of remobilization (Kar *et al*., 2008).Generally, there was a decrease in concentration down the river probably due to remobilization of heavy metals back to the water and uptake by plants along the river (WHO, 2008; Kar *et al*., 2008).

Comparable Mn concentrations have been obtained a concentration range of 1598.33 to 4322.83 mg/kg of Mn in sediment from Nairobi River were reported (Kage, 2003). Constant monitoring of levels of contamination to assess the impact of heavy metals in the aquatic system was, however, recommended. The results are comparable probably because Nairobi River is a tributary of Athi River in the upper Athi River basin (Kage, 2003).

4.2.1.4 Zinc (Zn) in sediments during the dry season

The mean concentrations of Zn from sediments during the dry season are recorded in Table 4.3. The concentration of zinc was found to range between 20.73 and 46.98 mg/kg DW. The levels of Zn in sediments sampled from all the sampling stations did not exceed the recommended limit of 123 mg/kg. Sediments are,however, known to accumulate more heavy metals with time that might be remobilized back to the water and to the food chain (Kar *et al*., 2008; WHO, 2008). While Zn is an essential element to plants and living organisms including human beings, prolonged exposure to high intakes of zinc results in copper and iron deficiency and subsequent anaemia (Reilly, 2002).

Significant differences were also reported in the levels of Zn between the sampling stations with station 4 (46.98 mg/kg) recording significantly high levels, $P<0.0001$. Sampling station 4 was located past Ruiru coffee plantations that might emit zinc compounds from either natural sources, or probablyfrom agricultural runoff where phosphate fertilizers are used(Awofolu*et al.*, 2005). Sampling station 10 that recorded significantly lowconcentration P(0.0001) and located downstream could have resulted inremobilization of heavy metals back to the water and uptake by plants along the river (WHO, 2008; Kar *et al*., 2008).

Higher Zn concentrations than the current study have been reported from a number of rivers (Kage, 2003; WHO, 2003;Alaa and Osman, 2010; Agatha, 2010). Zinc mean concentration of 91.5 to 307 mg/kg DW were recorded in sediments from Nile River during the dry season, 34.61mg/kg from Forcados River's sediments and 126.33-307.00 mg/kg from Nairobi River's sediments(Kage, 2003; Alaa and Osman, 2010; Agatha, 2010). Based on the data and toxicity of Zn, constant monitoring was recommended to protect mankind who uses the water and fish from the contaminated rivers.

4.2.1.5 Cadmium (Cd) in sediments during the dry season

The mean concentrations of Cd are recorded in Table 4.3. The concentrations of Cd obtained in sediments samples ranged between 0.05 and 1.50 mg/kg DW. In sampling station 2, 3, 4and 6,the concentrations were found to be higher than 0.6 mg/kgthe recommended limit for Cd in sediments (WHO, 2003). While the levels of Cd in sediment sampled from the other sampling stations did not exceed this recommended limit, the element is toxic and ingestion can rapidly cause feelings of nausea, vomiting, abdominal cramp and headache, as well as diarrhoea and shock (Reilly, 2002). It was also found that Cd varied significantly between and within the sampling stations ($P<0.05$) with sampling stations 6 (1.50 mg/kg DW) and 10 (0.05 mg/kg DW) recording significantly high and low Cd concentrations $P<0.0001$, respectively.Sampling station 6 was downstream of RuiruTownwhere the elevated Cd levels was attributed to car wash, industrial effluent and urban waste (WHO, 2008;Alaa and Osman, 2010;Abdel-Baki*et al*., 2011). Sampling station 10 with the lowest Cd concentration in sediments may be attributed to remobilization of heavy metals back to the water and uptake by plants along the river (Öztürk *el al*., 2009).

Comparable concentrations of Cd in sediments with the current study have been recorded from a number of rivers. Cadmium concentration range of 0.4-0.7 mg/kg of sediments from River Nile and 0.072 mg/kg from Wadi Hanifah River have been recorded (Alaa and Osman, 2010;Abdel-Baki*et al*., 2011). These concentrations were attributed to variations in mud present and increase in Cd metal rich urban effluents draining into River Nile (Alaa and Osman, 2010).Heavy metal contamination in sediments can affect the water quality and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem (Fernandes *et al*., 2007; Abdel-Baki*et al*., 2011).

4.2.1.6 Chromium (Cr) in sediments during the dry season

The mean concentrations of chromiumfor the dry season are recorded in Table 4.3. The concentration of Cr was found to range between 0.69 and 7.33mg/kg DW. Though the levels were below the recommended limit by FAO/WHO of 37.5mg/kg DW for Cr in sediment, increased levels can affect the water quality and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem (Reilly, 2002; Fernandes *et al*., 2007). It was also found that all the sampling stations recorded Cr mean levels that were significantly different $P<0.0001$. Sampling station 5 (7.33 mg/kg) and sampling station 1 (0.69 mg/kg) recorded significantly high and low concentrations $P<0.0001$, respectively.The significantly high concentration in sampling station 5 that was located downstream of Ruiru town could beattributed to car wash, industrial and urban waste (Kithiia, 2006). Sampling station 1 with significantly low Cr concentration $P<0.0001$ was located in the upper part of Athi river town and possibly had not received industrial or residential waste.

Comparable Cr levels with the current study have been reported.In the Wadi Hanifah River's sediment samples, the average value of Crwas 9.500 mg/kg DW (Abdel-Baki*et al*., 2011). Sediments act as the most important reservoir or sink of metals and other pollutants in the aquatic environment (Gupta *et al*., 2009). Heavy metal contamination in sediments can affect the water quality and bioaccumulation of metals in aquatic organisms, resulting in potential long-term implication on human health and ecosystem (Fernandes *et al*., 2007). Sediments from Wadi Hanifah contained very high significant amounts of chromium when compared with their concentration in water (0.006mg/kg) and fish (0.386mg/kg)(Abdel-Baki*et al*., 2011).A constant monitoring program to assess the impact of Cr in the ecosystem was therefore recommended.

4.2.2 Concentration of heavy metals in sediments during the wet season

Sediment samples were obtained from 10 sampling stations along the Mbagathi and Ruiru tributaries of Athi River. The mean levels of Pb, Ni, Mn, Zn, Cd and Cr in the sediments obtained in the dry season are presented in Table 4.4.

Table 4.4: Mean concentrations (mg/kg DW) of heavy metals in sedimentsduring the wet season (Mean±Sd)

	Sampling stations										
	1	2	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**P-value**
	Concentration ($\bar{x}$±Sd)										
Pb	49.48±1.64^{de}	51.08±1.89^{e}	35.54±1.45^{b}	42.15±1.94^{cd}	49.67±1.68^{de}	45.04±0.79^{cde}	46.25±1.94^{cde}	40.58±0.41^{bc}	23.87±3.90^{a}	28.71±1.10^{a}	<0.0001
Ni	0.89±0.17^{bc}	0.45±0.10^{ab}	0.22±0.05^{a}	0.69±0.06^{ab}	0.16±0.06^{a}	0.74±0.24^{ab}	2.21±0.29^{d}	0.37±0.20^{ab}	0.95±0.38^{bc}	1.39±0.06^{c}	<0.0001
Mn	1269.36±12.94^{f}	1294.01±8.05^{f}	824.76±60.97^{cd}	1084.42±65.15^{ef}	1068.92±100.43^{ef}	930.88±54.94^{de}	601.71±2.64^{bc}	418.38±34.54^{ab}	280.88±10.46^{a}	654.78±105.46^{c}	<0.0001
Zn	10.98±2.96^{a}	13.89±1.16^{b}	14.23±0.25^{a}	29.17±4.85^{b}	50.79±0.50^{c}	36.37±0.12^{b}	36.92±0.48^{b}	28.54±2.10^{b}	27.71±0.60^{b}	26.56±0.33^{b}	<0.0001
Cd	0.67±0.09^{a}	0.95±0.09^{a}	0.68±0.12^{a}	0.71±0.18^{a}	0.81±0.37^{a}	1.81±0.19^{b}	0.69±0.30^{a}	0.69±0.25^{a}	0.59±0.17^{a}	0.48±0.12^{a}	0.001
Cr	2.54±0.45^{b}	3.69±0.41^{b}	1.08±0.24^{a}	3.15±0.25^{b}	5.04±0.44^{c}	3.33±0.08^{b}	3.50±0.26^{b}	3.13±0.11^{b}	1.25±0.37^{a}	1.04±0.13^{a}	<0.0001

*Means values followed by the same small letter within the same row are not significantly different at 95% confidence level

All the heavy metals analysed in sediments during the wet season were detected and their concentrations differed significantly between the sampling stationsP<0.05. The presence of these heavy metals in the sediments could be attributed to discharge of industrial effluents, municipal and residential wastes (Obasohan, 2008; Kar *et al*., 2008).

4.2.2.1 Lead(Pb) in sedimentsduring the wet season

Leadmean concentrations recorded during wet season are presented in Table 4.4**.**Lead concentrations recorded ranged from 23.87 to 51.08 mg/kg with all the sampling stations except stations 9 and 10 recording levels that were higher than the recommended limit of 35 mg/kg for Pb in sediment (WHO, 2003). This means that pollution was high and poses a threat to the ecosystem and indirectly to man through food chain(Muwanga and Barifaijo, 2006).Some effects of Pb poisoning include deficiency in cognitive function due to destruction of the central nervous system. Exposure to high Pb levels can severely damage the brain and kidneys, cause miscarriage in pregnant women, damage the organs responsible for sperm production in men and it may ultimately cause death (ATSDR, 2002).

The values in all the sampling stations were significantly different with sampling station 2 recording the highest Pb mean concentrations P<(0.0001). Thesehigh concentrations could possibly be due to runoff, from garage and car washes, use of pesticides, fertilizers and discharge of untreated urban and industrial waste(Awofolu *et al.,* 2005).Generally, the Pb concentrations indicated a decrease downstream which was attributed to a big part of the heavy metal in sediments being released back to water compartment in the process of remobilization (Kar *et al*., 2008).

The ten sampling stations recorded significantly different concentrations with sampling station 3 and 4 recording significantly high values while sampling station 10 recorded significantly low concentration P(0.0001). The significantly low concentration P(0.0001) in sampling station 10 located downstream could be attributed to dilution effect (Kar *et al*., 2008). The significantly high P(0.0001) Pb concentrations from the sampling stations 3 and 4 located before Ruiru town was attributed to agricultural and residential effluent (Kithiia, 2006; Mwegoha and Kihampa,2010).

Some studies have reported different ranges of Pb concentrations compared to the current study from different rivers.Concentrations ranging between 3.1 and 76.9 mg/kg and between 0.040 and 0.067 mg/kg were recorded from Nileand Tyume Rivers(Awofolu *et al.,* 2005; Alaa and Osman, 2010).The wide ranges of metal concentrations that were recordedwas attributed to variations in mud present and increase in Pb metal rich urban effluents draining into River Nile (Alaa and Osman, 2010). Awofolu*et al.,* (2005) reported that the sediment could be an influential factor on the level of Pb in river waterhence continual assessment is highly essential.

4.2.2.2 Nickel (Ni) in sedimentsduring the wet season

The results for the analysis of Ni in sediments for the wet season are recorded in Table 4.4and the levels were found to range from 0.16-2.21mg/kg DW.Though Ni limits have not been documented for sediments, Ni compounds, except for metallic Ni, have been classified as carcinogenic to humans. Among the known health-related effects of Ni are skin allergies, lung fibrosis, variable degrees of kidney and cardiovascular system poisoning and stimulation of neoplastic transformation (ATSDR, 2005).

When Ni from different sampling stations was compared statistically, there was significant difference with sampling station 7 recording significantly high value of 2.21 mg/kg P<(0.0001). Sampling station 7 was downstream of Ruiru River and received industrial and urban effluent from Ruiru town (Kithiia, 2006; Mwegoha and Kihampa,2010).It was therefore concluded that constant monitoring of levels of contamination was necessary to assess the impact of heavy metals in the aquatic system.

Higher concentrations than the current study have been recorded in some rivers. Ni mean levels of42.37mg/kg DW from Forcados Riverand a range between 0.06 and 258.17 mg/kg DW from Buriganga River were higher than the current study (Ahmad *et al*., 2009; Agatha, 2010). Possible sources of Ni in surface water leading to accumulation in the sediment are from anthropogenic activities like combustion of fossil fuels, old battery wastes, components of automobiles, old coins, and many other items containing stainless steel and other Ni alloys (Awofolu *et al*., 2005).

4.2.2.3Manganese (Mn) in sedimentsduring the wet season

Manganese concentrations recorded during wet season are in Table 4.5 and the values were found to range from 280.88-1294.01 mg/kg DW. Significance difference was observed between the sampling stations, with sampling station 2 recording the highest levels of 1294.01 mg/kg DW P<0.0001. This indicated that the sediment had accumulated manganese whose sources could have been runoff from the large coffee plantations, garages and car washes, rocks and soils directly exposed to surface water (APHA *et al.*, 2005;Alaa and Osman, 2010).There was also a general decrease in concentration down the river with sampling station 9 recording significantly

low Mn concentration (P<0.0001)probably due to remobilization of heavy metals back to the water and uptake by plants along the river (WHO, 2008; Kar *et al*., 2008).

Manganese has also been reported from other studies with some levels that were comparable to the current study. A concentration that ranged from 139.8 to 351.8 from River Nileand 886.89mg/kg fromNorthern Delta Lake were recorded. These concentrations were attributed to variations in mud present and increase in urban effluents draining into River Nile (Samir and Shaker, 2008; Alaa and Osman, 2010). Exposure to the toxic manganese may lead to Mnrelated complications that include psychiatric and motor disturbances, termed manganism which has occurred in people employed in the production and processing of Mn alloys (Nussey *et al.*, 2000). Constant monitoring of levels of contamination to assess the impact of heavy metals in the aquatic system was, however, recommended.

4.2.2.4 Zinc (Zn) in sedimentsduring the wet season

Zinc concentrations recorded during wet season are in Table 4.4and the values werefound to range from 10.98-50.79 mg/kg DW and these were within the WHO's recommended limit of 123 mg/kg for sediment.Sediments are known to accumulate heavy metals and with time might be remobilized back to the water and follow the food chain (WHO, 2003; Kar *et al*., 2008). The ten sampling stations recorded significantly different concentrations with sampling station 5(50.79 mg/kg) recording significantly high levels P<0.0001. Sampling station 5 was down past Ruiru town where industrial effluent, runoff from coffee plantations and urban waste can contribute to these levels (Kithiia, 2006).

Contrary to the levels reported in this study, sediment has been found to have varying levels of Zn in a number of rivers (Kage, 2003; WHO, 2003; Alaa and Osman, 2010; Agatha, 2010). Levels ranging between 91.5 and 307 mg/kg DW in sediments from River Nile during the dry season, 34.61mg/kg from Forcados River and values that ranged between 126.33 and 307.00 mg/kg for sediments of Nairobi River constitute immediate hazard to aquatic fauna and human consumers (Oguzie, 2003; Kage, 2003; Oguzie and Izevbigie, 2009;Agatha, 2010). Zinc salts are intestinal irritants and can cause nausea, abdominal pain and damage nerve receptors in the nose, which can cause anosmia(Johnson *et al*., 2007; Kar *et al*., 2008;Safty *et al*., 2008).Constant monitoring of levels of contamination to assess the impact of heavy metals in the aquatic system was therefore recommended.

4.2.2.5 Cadmium (Cd) in sedimentsduring the wet season

The concentration of Cd was found to range between 0.48 and 1.81 mg/kg DW. In all the sampling stations except sampling stations 9 and 10, the levels were found to be higher than 0.6 mg/kg recommended limit for sediment (WHO, 2003). These high values pose immediate health hazard that may result in complications associated with Cd like Itai-itai disease, with effects on vital organs like liver, placenta, kidneys, lungs, brain and bones (Reilly, 2002). There were also significant differences in the levels of Cd reported between the sampling stations, with sampling station 6 recording significantly high concentration of 1.81 mg/kg DW and sampling station 10 recording significantly low concentration of 0.48 mg/kg $P<0.001$. Sampling station 6 was down past Ruiru town where both industrial effluent and urban waste can be attributed to these high levels (WHO, 2008; Alaa and Osman, 2010;Abdel-Baki*et al*., 2011). Sampling station 10 was

downstream where concentration decreased due to remobilization to the water body (Kar *et al*., 2008).

Lower Cd levels than those reported in the current study have been reported (Awofolu *et al.,* 2005). The levels of Cd obtained in sediment samples from Tyume River varied between trace and 0.005 mg/kg which were also within the recommended limit,did not constitute immediate hazard to aquatic fauna and human consumers (Awofolu *et al.,* 2005). Since studies indicate that Cd accumulates in sediment,and is toxic even at low levels, constant monitoring of levels of contamination to assess the impact of the heavy metal in the aquatic system was however recommended as target organs include liver, placenta, kidneys, lungs, brain and bones (Reilly, 2002).

4.2.2.6 Chromium (Cr) in sedimentsduring the wet season

Sediment concentrations for Cr during wet season are recorded in Table 4.4 and the levels were found to range between 1.04 and 5.04mg/kg DW. Though the levels were below the recommended limit of 37.5 mg/kg for Cr in sediments by WHO,hexavalent Cr is very toxic and mutagenic when inhaled and is a known human carcinogen, and breathing high levels can cause irritation to the lining of the nose, runny nose and breathing problems and exposure can also cause damage to liver, kidney circulatory and nerve tissues (Dayan and Paine, 2001). Statistically, all the sampling stations were significantly different, with sampling station 5 (5.04 g/kg) and 10 (1.04mg/kg) recording significantly high and low concentrations$P<0.0001$ respectively. Sampling station 5 was located near Ruiru town whose levels could be attributed to industrial effluent and urban waste (Kithiia, 2006). Sampling station 10 was located downstream

with significantly low concentration P(0.0001) possibly due to dilution effect and self-purification of the river waters as the concentration has been reported to decrease downstreamduring the wet season(Kithiia, 2006).

Concentrations that were higher than the current study have been reported from a number of rivers (Ahmad *et al*., 2009; Oguzie and Izevbigie, 2009). Chromium mean concentrations of 0.021 mg/kg from sediments of Ikpoba River and concentration of Cr that ranged from 60.09 to 91.02 mg/kg from Shitalakhya River were found to be lower than Cr concentration that ranged from118.63 to 218.39 mg/kg from Buriganga River (Ahmad *et al*., 2009; Oguzie and Izevbigie, 2009).These concentrations were also higher than the recommended limit of 35.7 mg/kgfor Cr in sediments by WHO exposing mankind to Cr related toxic effect likedamage to liver, kidney circulatory and nerve tissues (Dayan and Paine, 2001;WHO, 2003). Constant monitoring of levels of contamination to assess the impact of heavy metals in the aquatic system was however recommended.

4.3Concentration of heavy metals in water

Water was analysed for heavy metals during wet (April and May) and dry (June and July) seasons and the results are discussed.

4.3.1 Concentration of heavy metals in water during the dry season

Water samples were obtained from 10 sampling stations along the Mbagathi and Ruiru tributaries of Athi River. The mean levels of Pb, Ni, Mn, Zn, Cd and Cr in the water obtained in the dry season are presented in Table 4.5.

Table4.5: Mean concentrations (mg/l)of heavy metals in water duringthe dry season (Mean±Sd)

	Sampling stations										
	1	2	3	4	5	6	7	8	9	10	P-value
	Concentration ($\bar{x}$±Sd)										
Pb	0.032±0.002^{c}	0.034±0.003^{c}	0.005±0.001^{ab}	0.015±0.002^{b}	0.035±0.002^{c}	0.015±0.005^{b}	0.007±0.002^{ab}	0.010±0.004^{ab}	0.004±0.001^{a}	0.005±0.001^{ab}	<0.0001
Ni	0.040±0.006^{a}	0.034±0.005^{ab}	0.008±0.002^{a}	0.032±0.005^{ab}	0.025±0.002^{abc}	0.040±0.006^{c}	0.020±0.007^{abc}	0.018±0.005^{abc}	0.012±0.007^{abc}	0.018±0.003^{abc}	<0.0001
Mn	0.928±0.083^{bc}	0.773±0.051^{a}	0.538±0.016^{a}	0.553±0.014^{a}	0.702±0.004^{ab}	0.772±0.039^{abc}	0.987±0.036^{c}	1.048±0.088^{c}	0.947±0.024^{bc}	0.533±0.099^{a}	<0.0001
Zn	0.016±0.003^{ab}	0.036±0.001^{c}	0.035±0.002^{c}	0.008±0.002^{a}	0.006±0.003^{a}	0.016±0.003^{ab}	0.055±0.003^{d}	0.023±0.008^{b}	0.002±0.001^{a}	0.010±0.005^{ab}	<0.0001
Cd	0.005±0.001^{bc}	0.010±0.001^{d}	0.001±0.000^{a}	0.001±0.000^{a}	0.008±0.002^{cd}	0.004±0.001^{ab}	0.002±0.001^{ab}	0.003±0.001^{ab}	0.001±0.000^{a}	0.001±0.000^{a}	<0.0001
Cr	0.068±0.051	0.035±0.006	0.010±0.003	0.005±0.002	0.030±0.004	0.015±0.006	0.003±0.002	0.003±0.002	0.002±0.002	0.005±0.002	0.385

*Means values followed by the same small letter within the same row are not significantly different at 95% confidence level

During the dry season, water was found to contain all the heavy metals with most of the elements concentrations varying significantly between the sampling stations ($P<0.05$). Manganese mean concentrations were found to range from 1.048-0.055 mg/l while, cadmium's concentrations ranged from 0.01 to 0.001 mg/l and leads mean concentrations were found to range from 0.004 to 0.015mg/l

4.3.1.1 Lead (Pb) in water during the dry season

The concentration of Pbin water was found to range from 0.035-0.004 mg/l. Leadvalue were found in six sampling stations to be higher than 0.01 mg/l, recommended limit of Pb in drinking water(WHO, 2008). This makes the water unsuitable for human consumption as Pb is known to be toxic even at low levels with resultant ill-health effects as chronic exposure has been linked to growth retardation in children **(**Awofolu *et al.*, 2005; WHO, 2008).Significant difference was evident from all the sampling stations, with sampling station 5 down Ruiru River recording the highest Pb mean value of 0.035 mg/l which was attributed to untreated industrial effluent (WHO, 2008). A general decrease in the mean concentration of Pb was evident down the river and this could be due to dilution effect from runoff as well as absorption by plants and sediments in the river (Kithiia, 2006; Kar *et al*., 2008).

Studies of water from Ikpoba River, and Nairobi River recorded mean Pblevels of 0.035mg/l and 0.1 mg/l that were comparable to the current studies but above the recommended limit of 0.01mg/l of Pb in drinking water (Kithiia, 2006; Oguzie and Izevbigie, 2009).Based on these results it was therefore recommended that an evaluation program be set up to constantly monitor

the levels of heavy metals in order to protect people using the river water against possible contamination.

4.3.1.2 Nickel (Ni) in waterduring the dry season

Results from analysis of Ni are recorded in Table 4.6 which, shows that Ni mean concentrations ranged from 0.04 to 0.008 mg/l. While all the sampling stations recorded Ni mean values that were below the recommended limit of 0.07mg/l, elevated levels in drinking water have been reported to cause sub-lethal effects such as lung fibrosis, variable degrees of kidney and cardiovascular system poisoning (Nussey *et al.*, 2000; Kasprzak *et al.,* 2003; WHO, 2008).

It was also found that Ni mean levels differed significantly in all sampling stations $P<0.05$, with sampling station 6 (0.040mg/l) recording significantly high levels while the lowest was from sampling station 3 (0.008 mg/l). Sampling station 6 was down stream of River Ruiru with industrial effluent and urban waste likely to increase Ni concentration (Mwegoha and Kihampa, 2010).

Higher Ni meansvalues than those reported in the current study that ranged from 0.201 to 1.777mg/l in water from Tyume River have been reported (Awofolu*et al.*, 2005). Higher concentrations than0.07mg/l, the WHO recommended limit of drinking water were obtained. This was attributedto anthropogenic sources such as combustion of fossil fuels, old battery wastes, components of automobiles, old coins, Ni alloys and many other items containing stainless steel.

4.3.1.3 Manganese (Mn) in water during the dry season

The mean levels of Mn recorded are listed in Table 4.5 and these values ranged from 0.533-1.048 mg/l. In all the sampling stations, Mn was found to be higher than 0.4 mg/l the recommended limit for Mn in drinking water (WHO, 2008). This means that the water was polluted and unsuitable for human use as far as Mn is concerned.This exposes the population using Athi river water to a threat of Mn related problems like neurological damage and motor disturbances (Nussey *et al.*, 2000; Reilly, 2002).

All the sampling stations recorded Mn concentrations that differed significantly with sampling station 8 (1.048 mg/l) recording significantly high levels while the lowest was from sampling station 10 (0.533 mg/l) $P<0.0001$. The high levels could have been due to dissolution from impending rocks as the rocks and soils directly exposed to surface water are the largest natural sources as well as discharge of various treated and untreated liquid wastes to the water body (APHA *et al*., 2005; WHO, 2008; Alaa and Osman, 2010).

Manganese concentrations that are in agreement with those reported by the current study have been recorded from other rivers. Concentrations ranging from 0.033-0.14mg/l from River Nile and mean levels of 2.5 mg/l from Nairobi River have been recorded (Wachira, 2007; Alaa and Osman, 2010).These were attributed to inputs from rocks and soils directly exposed to surface water and discharge of various treated and untreated liquid wastes to the water body, industrial wastes and atmospheric inflow of dust (Ibrahim and Tayel, 2005;Wachira, 2007; Alaa and Osman, 2010).Based on the results obtained for the two tributaries, the river is highly polluted

making the water unfit for human use and assessment of rocks and soil from the area is essential as well as controlling discharge of untreated waste to the river.

4.3.1.4 Zinc (Zn) in water during the dry season

Zinc mean concentrations were analysed for the dry season and the mean levels are recorded in Table 4.5 and the values ranged from 0.002-0.055 mg/l. All the sampling stations recorded Zn mean concentrations that didn't exceed the recommended limit of 3mg/l for Zn in drinking water meaning that the water was safe for human use as far as Zn is concerned (WHO, 2008). There were, however, significant differences in the levels of Zn between the sampling stations with station 7 (0.055mg/l) recording significantly high levels while the lowest was from sampling station 9 (0.002 mg/l) $P<0.0001$. Sampling station 7 was located below Ruiru Town, whose high concentration was attributed to untreated urban, industrial and residential effluent (Kithiia, 2006). Zinc metal concentrations also showed a general decrease in the mean levels down the river that was as a result of dilution effect from run off as well as absorption by plants and sediments in the river(Kithiia, 2006; Kar *et al*., 2008).

Zinc concentrations that were higher than those found by present study have been reported(Kar *et al*., 2008; Agatha, 2010). Concentrations of 0.085 and78.25 mg/l from Ganga and Forcados Rivers that were higher than the reported values in the present studywere recorded (Kar *et al*., 2008; Agatha, 2010). Agatha (2010) observed that the water was contaminated with Zn and could be toxic to other aquatic fauna and poisonous to human consumers and recommended constant monitoring of levels of contamination to assess the impact of the heavy metal in the aquatic system.

4.3.1.5 Cadmium (Cd) in waterduring the dry season

The results of analysing water samples for Cd are recorded in Table**4.**5 showing values that ranged from 0.001 to 0.010 mg/l. The Cd mean concentrations recorded in five (5) sampling stations were higher than 0.003 mg/l, the recommended limit for drinking water (WHO, 2008). These high levelscould be attributed to discharge of untreated sewage, industrial effluent or disposal of urban waste to the river form Athi river town. All the sampling points gave results that were significantly different with sampling station 2 (0.01 mg/l) having the highest concentration and sampling stations 3, 4,9 and 10 recording statistically similar low concentrations of 0.001 mg/l $P<0.0001$.

Findings that had results higher than those reported by the current study have been reported from other rivers (Samir and Shaker, 2008; Agatha, 2010).Cadmium mean concentrations of 0.019 mg/l, 10.25 mg/land 0.002 mg/lfromNorthern delta lake, Forcados and GangaRivers were higher than the permissible limit of 0.003 mg/l for drinking water by the WHO (Samir and Shaker, 2008;Kar *et al*., 2008; WHO, 2008;Agatha, 2010). The high levels of Cd in water could be attributed to industrial and agricultural discharge (Awofolu *et al*., 2005; Samir and Shaker, 2008;Alaa and Osman, 2010). From the results, it is therefore recommended that constant monitoring of levels of contamination is necessary to assess the impact of heavy metal in the aquatic system.

4.3.1.6 Chromium (Cr) in water during the dry season

The mean levels of Cr for all considered sampling stations are recorded in Table 4.6 showing values that ranged from 0.002 to 0.068 mg/l. These Cr mean levels were lower than the

recommended limit of 0.05 mg/l for Cr in drinking water except sampling station 1 with Cr mean level of 0.068 mg/l (WHO, 2008). This means that consumption of water from the selected Athi River tributaries is not safe since hexavalent Cr is very toxic and mutagenic when inhaled and is a known human carcinogen, where long term exposure can cause damage to liver, kidney circulatory and nerve tissues, as well as skin irritation (Dayan and Paine, 2001). Constant monitoring and control program need be instituted to protect the high population down the river using the river water.

Chromium mean concentrations that were above the current study have been reported (Wachira, 2007; Abdel-Baki*et al*., 2011).Studies from Wadi Hanifah and Nairobi Riversrecorded Cr mean concentrations of 0.006mg/l and 0.02 mg/l,respectively which were not higher than 0.05mg/l the recommended limit for Cr in drinking(Wachira, 2007; WHO, 2008; Abdel-Baki*et al*., 2011). These low concentrations did not pose immediate hazard to the population using these river's water.

4.3.2 Heavy metal concentrations for water during wet seasons

Water was obtained from the ten sampling stations along the Mbagathi and Ruiru tributaries of Athi River during the wet seasons. The mean levels of Pb, Ni, Mn, Zn, Cd and Cr obtained are presented in Table 4.6.

	Sampling stations										
	1	2	3	4	5	6	7	8	9	10	P-value
	Concentration ($\bar{x}$±Sd)										
Pb	0.016±0.004^{ab}	0.022±0.005^{ab}	0.017±0.003^{ab}	0.010±0.002^{a}	0.010±0.002^{a}	0.040±0.004^{cd}	0.009±0.003^{a}	0.030±0.007^{ab}	0.047±0.008^{d}	0.007±0.001^{a}	<0.0001
Ni	0.018±0.002^{ab}	0.014±0.003^{ab}	0.025±0.003^{b}	0.020±0.002^{ab}	0.025±0.004^{b}	0.023±0.008^{ab}	0.017±0.003^{ab}	0.062±0.002^{c}	0.007±0.003^{a}	0.022±0.006^{ab}	<0.0001
Mn	0.831±0.010^{cd}	0.888±0.010^{d}	0.726±0.009^{bcd}	0.589±0.090^{b}	0.187±0.054^{a}	0.230±0.008^{a}	0.560±0.070^{b}	0.555±0.048^{b}	0.652±0.041^{b}	0.681±0.012^{bc}	<0.0001
Zn	0.123±0.012^{a}	0.103±0.011^{a}	0.056±0.006^{a}	0.047±0.004^{a}	0.053±0.015^{a}	0.046±0.007^{a}	0.076±0.010^{a}	0.141±0.003^{a}	0.095±0.016$^{B\,a}$	0.695±0.288^{b}	0.002
Cd	0.002±0.000^{ab}	0.004±0.001^{c}	BDL	0.001±0.000^{a}	0.004±0.002^{bc}	0.001±0.001^{ab}	0.001±0.001^{a}	0.001±0.001^{ab}	0.001±0.000^{a}	BDL	0.005
Cr	0.003±0.001	0.002±0.001	0.001±0.001	0.002±0.001	0.003±0.002	0.001±0.001	BDL	0.001±0.001	0.001±0.001	0.001±0.000	0.71

Table 4.6: Mean concentrations (mg/l)of heavy metals in waterduring the wet season (Mean±Sd)

BDL= Below Detection Limit

*Means values followed by the same small letter within the same row are not significantly different at 95% confidence level

During the wet season, water was found to contain all the heavy metals. It was also found that most of the elements varied significantly between the sampling stations ($P<0.05$). The presence of these heavy metals in the water could be attributed to discharge of industrial effluents and municipal wastes, geology of river bed and catchment area (Obasohan, 2008; Kar *et al*., 2008).

4.3.2.1 Lead (Pb) in water during wet seasons

The mean Pb concentrations recorded during wet season are presented in Table 4.6 and the values were within the range of 0.047-0.007 mg/l. The Pb mean concentration in all the sampling stations except sampling station 7 (0.009 mg/l) and 10 (0.007mg/l) were higher than the WHO recommended limit of 0.01 mg/l of Pb in drinking water (WHO, 2008). The high levels were attributed to the discharge of untreated industrial agricultural and urban effluent to the river. These indicates a high pollution in the river water and that its use poses a high health risk of Pb poisoning as the element is known to be toxic even at low levels **(**Mwegoha and Kihampa, 2010). Sampling station 10 was downstream and therefore Pb concentrationswere observed to decrease downstream from pollution points which, was linked to dilution effect from runoff as well as absorption by plants and sediments in the river (Kithiia, 2006; Kar *et al*., 2008).

It was also observed that all the sampling stations recorded concentrations that significantly differed with station 9 (0.047 mg/l) recording significantly high levels while the lowest was from sampling station 10 (0.007 mg/l) $P<0.0001$. Sampling station 9 was downstream of Ruiru River and both industrial effluent and residential waste were contributed to these levels (Mwegoha and Kihampa, 2010).

Higher Pb mean concentrations (0.05 mg/l) than those reported by the current study which were also higher than the recommended limit of 0.01mg/l for drinking water (Wachira, 2007; WHO, 2008). Wachira (2007) reported that the water from Nairobi River was unsuitable for domestic use and attributed the higher level to discharge of untreated industrial and urban effluent to the river. From the findings, it was recommended that constant monitoring of levels of contamination to assess the impact of heavy metals in the aquatic system was necessary.

4.3.2.2 Nickel (Ni) in waterduring wet seasons

The mean levels of Ni for the ten (10) considered sampling stations are recorded in Table 4.7. During this season, Ni mean levels ranged from 0.007 to 0.062 mg/l with all the sampling stations recording results that were below the 0.07mg/l the recommended limit for Ni in drinking water, which means that the water in Athi river selected tributaries was safe for human use as far as Ni contaminant is concerned (WHO, 2008). It was also found that, Ni mean concentrations from all the sampling stations, gave significantly different results, with sampling station 8 (0.062 mg/l) recording significantly high levels while the lowest was from sampling station 9 (0.007 mg/l) $P<0.0001$. The variation of these concentrations was attributed to industrial effluent from Ruiru town and residential waste.

Studies of the heavy metal in water from some rivers have indicated varying profiles in Ni concentrations compared to the current study (Wachira, 2007; Oguzie and Izevbigie, 2009). Concentrations of 0.03 and 0.01 mg/l reported from Nairobi and Ikpoba Rivers were lower than both thevalues reported by the current study and the recommended limit of 0.07 mg/l (Wachira

2007; Oguzie and Izevbigie, 2009). Oguzie and Izevbigie (2009) reported that the anthropogenic sources as the major cause of pollution in the Nigerian aquatic environment. The difference in concentration with the current study was attributed to differences in geology and anthropogenic activities.

4.3.2.3 Manganese (Mn) in water during wet seasons

The mean concentrations of Mn for the ten (10) considered sampling stations are recorded on Table 4.7 showing valuesthat rangedbetween 0.187-0.888 mg/l. The mean concentrations were found to be higher than the recommended limit (0.4 mg/l) for Mn in drinking water in all the sampling stations except sampling station 5 (0.187 mg/l) and 6 (0.230 mg/l) (WHO, 2008). The higher levels will imply health hazard that could result in Mn related illnesses like neurological damage and motor disturbances (Reilly, 2002). All the sampling stations were also found to record Mn mean concentrations that were significantly different $P<0.05$. Sampling station 10 (0.681 mg/l) recordedsignificantly high Mn concentrations while sampling station 5 (0.187 mg/l) recorded significantly low concentrations during the wet season $P<0.0001$. The high concentration was attributed to dissolution from impending rocks as well as runoff from Ruiru Town, Athi river town and surrounding industries and other residential effluents all directing their effluent to Athi River (Ibrahim and Tayel, 2005; Alaa and Osman, 2010).

Manganese concentrations have also been recorded from other rivers with varying concentrations compared to the current study (Wachira, 2007; Kar *et al.*,2008;Alaa and Osman, 2010). Manganesevalues that ranged between 0.033 and 0.14mg/l from Nile River were lower than 2.5

and 0.423 mg/l Mn concentrations from Nairobi and Ganga Rivers' water during wet season (Wachira, 2007; Kar *et al.*,2008; Alaa and Osman, 2010).These levels from Nairobi and Ganga rivers were in agreement with the current study and also higher than the recommended limits of 0.4 mg/l for Mn in drinking water. As a result, these Mn concentrationspose a risk of manganese related illnesses to the population using the water and aquatic life as food (Wachira, 2007; Kar *et al.*,2008;WHO, 2008;Alaa and Osman, 2010). This excess heavy metal load was attributed to the discharge of industrial effluents, municipal wastes, geology of river bed and catchment area(Wachira, 2007; Kar *et al.*,2008; Alaa and Osman, 2010). Constant assessment of manganese to control its discharge from the river was recommended.

4.3.2.4 Zinc (Zn) in waterduring wet seasons

The mean levels of Zn for the ten sampling stations are recorded on Table 4.8.The values were in the range of0.046-0.695 mg/l which means that all the sampling stations recorded Zn mean levels that were below the recommended limit of 3 mg/l Zn in drinking water (WHO, 2008). However, metals from river water could be a contributing source to the levels in vegetables grown by the small scale farmers and continual assessment is highly essential (Awofolu *et al*., 2005). Significant differences in the levels of Zn between the sampling stations were recorded with station 10 (0.695mg/l) having significantly high levels while the lowest was from sampling station 6 (0.046 mg/l) $P<0.05$. These variations were attributed to either discharge of untreated sewage, industrial effluent or disposal of urban waste and geology of river bend(Kar *et al*.,2008; Mwegoha and Kihampa, 2010;).A general decrease in the mean levels of zinc was evident down

the river and could be attributed to dilution effect from run off as well as absorption by plants and sediments in the river (Kithiia, 2006; Kar *et al*., 2008).

Slightly higher Zn concentrations than the current study but lower than the recommended limit were recorded from River Ganga during wet season with a mean of 0.716 mg/ which was attributed to asudden rainfall followed by high river discharge from upstream environment (Kar *et al*.,2008).

4.3.2.5 Cadmium (Cd) in waterduring wet seasons

Cadmium mean concentration during the wet season ranged from ND to 0.004 mg/l with all the sampling stations recording levels that were below the recommended limit of 0.003 mg/l Cd in drinking water except sampling stations 2 and 5 with 0.004 mg/l each. Though the levels of Cd in most sampling stations were within the limit, the element is toxic even at low levels which can result to feelings of nausea, vomiting, abdominal cramp and headache, as well as diarrhoea and shock. About 15 mg of cadmium has been reported to bring these effects with target organs including liver, placenta, kidneys, lungs, brain and bones (Reilly, 2002). There was a decrease in the mean levels of Cd observed down the river and this was attributed to dilution effect from run off as well as absorption by plants and sediments in the river (Kithiia, 2006; Kar *et al*., 2008). Significant differencesin Cd concentrations were reported within the sampling stations, with sampling stations 2 and 5 recording the highest mean of 0.004 mg/l each while sampling stations 3 and 10 had ND concentrations. The high levels could be attributed to untreated urban and industrial effluent from Ruiru and Athi river towns.

Previous studies have reported levels of Cd in water from other rivers (Fatoki and Awofolu, 2003; Awofolu *et al*., 2005;Alaa and Osman, 2010). Cadmium concentrations that ranged between 0.002 and 0.02 mg/l from river Nile and between 0.030 and 0.044from Tyume River have been previously reported and these were higher than those reported by current study. These values were higher than the recommended limit of 0.003mg/l for Cd in drinking water (Fatoki and Awofolu, 2003; Awofolu *et al*., 2005; WHO, 2008; Alaa and Osman, 2010). Apart from natural sources, other probable sources of this metal in surface water could include leaching from Ni-Cd based batteries, runoff from agricultural soils where phosphate fertilisers are used, industrial wastes and atmospheric inflow of dust (Fatoki and Awofolu, 2003; Ibrahim and Tayel, 2005; Alaa and Osman, 2010). Based on the above findings, it was recommended that control measures should be taken to protect the population using this water against Cd poisoning.

4.3.2.6 Chromium (Cr) in water during wet seasons

The mean levels of Cr for all sampling stations under study are recorded in Table 4.7. The concentration of Cr was found to range from ND-0.003 mg/l and these were lower than the recommended limit of 0.05 mg/l for Cr in drinking water (WHO, 2008). While the levels of Cr in water do not exceed the recommended limit, the element is very toxic and mutagenic when inhaled and is a known human carcinogen, and breathing high levels can cause irritation to the lining of the nose, runny nose and breathing problems (Dayan and Paine,2001).

Chromium concentrations that ranged between 0.01 and 1.414 mg/l from Msimbazi river waterwere reported which were higher than the values reported in this study.This could be

attributed to the effluent into the streams that are loaded with pollutants from various industries including textile, which are known to contain Cr.It was also reported that the presence of heavy metals in water indicates the potential for pollution transfer from these media to the food chain (Mwegoha and Kihampa,2010).

4.4: Comparison of levels of heavy metals between Ruiru and Mbagathi tributaries

Pollution levels from the two selected Athi River tributaries (Ruiru and Mbagathi) were compared and the results were recorded in Table 4.7

Table 4.7: Comparison of levels of heavy metals in fish, sediments and water between Ruiru and Mbagathi rivers

	Fish			Sediment			Water		
Elements	Ruiru	Mbagathi	**p-value**	Ruiru	Mbagathi	**p-value**	Ruiru	Mbagathi	**p-value**
Pb	2.85±0.31	1.72±0.05	**0.016**	35.84±1.17	37.51±2.00	**0.441**	0.02±0.00	0.02±0.00	**0.015**
Ni	0.79±0.19	0.77±0.09	**0.942**	0.74±0.09	0.72±0.10	**0.883**	0.02±0.00	0.03±0.00	**0.031**
Mn	143.22±14.59	115.11±13.05	**0.224**	911.23±40.26	842.82±73.59	**0.377**	0.58±0.03	0.81±0.03	**<0.001**
Zn	50.57±4.11	49.15±2.56	**0.817**	36.91±1.34	21.91±1.38	**<0.001**	0.04±0.00	0.07±0.01	**<0.001**
Cd	1.08±0.09	1.41±0.11	**0.038**	0.88±0.10	0.64±0.08	**0.110**	0.00±0.00	0.00±0.00	**0.021**
Cr	0.03±0.01	0.04±0.03	**0.603**	3.95±0.25	2.53±0.29	**<0.001**	0.01±0.00	0.01±0.00	**0.40**

The results show differences in levels of heavy metals between the two rivers Ruiru and Mbagathi. Mean concentration of Pb in fish gills was significantly high ($P < 0.05$) in Ruiru river while Cd was significantly high ($P < 0.05$) in Mbagathi river. These could be attributed to urban, residential and industrial effluent, aspects that are manifested along these rivers (Awofolu*et al*., 2005). In sediments, the concentrations of Cr and Zn were significantly high ($P < 0.05$) in Ruiru River in comparison to Mbagathi River. Agricultural activities and effluents from residential and urban set ups are known to contribute to such levels (Awofolu*et al*., 2005; Alaa and Osman, 2010). Levels of Pb, Ni, Mn, Zn, and Cd in water were found to be significantly high ($P<0.05$) from Mbagathi River as compared to Ruiru River possibly due to the cement industries, residential and urban waste (Kithiia, 2006; Mwegoha and Kihampa,2010).

4.5:Correlation Analysis of metals in fish gills, sediments and water during dry season

Pearson correlation analysis of metals in tilapia fish gills, sediments and water during dry and wet season were performed to assess possible similar sources of metals. The heavy metals with positive correlation were considered to have similar sources (Moore and Attar, 2011). Results for the correlation analysis are shown in **Appendix V.**

Correlation analysis of metals during dry season shows that Ni in water had significantly positive correlation with Ni in sediments (0.332), while, Cr in water during dry season had a significant negative correlation with Cr from sediments(-0.277). Cadmium in water during dry season had also a significant positive correlation with Cd in sediment (0.227) during dry season. During wet season, Zn in water had a significant negative correlation with Zn in sediments (-0.418).

The possible sources of these metals in surface water apart from natural source include leaching from Ni-Cd based batteries and runoff from agricultural soils where fertilizers are used (Awofolu *et al.,* 2005).

4.6: Seasonal variations of elements

The seasonal variations (wet and dry seasons) of all the elements studied in fish, sediment and water were calculated and the results of the analysis are shown in Table 4.8.

Table4.8: Seasonal variations of elements in tilapia fish gills (N=48), sediments (N=120) andwater (N=120)

Elements	Dry season mean±SE	Wet season mean±SE	df	tcal	tcri
Fish					
Pb	2.43±0.25	2.30±0.24	46	0.375	2.013
Ni	0.52±0.09	0.88±0.19	46	1.719	2.013
Zn	37.37±1.94	62.06±3.41	46	6.286	2.013
Mn	117.59±18.65	141.18±4.16	25	1.234	2.060
Cd	1.31±0.10	1.32±0.09	46	0.115	2.013
Cr	0.04±0.02	0.02±0.00	25	0.918	2.064
sediment					
Pb	26.97±0.25	41.29±1.07	98	13.034	1.984
Ni	0.74±0.05	0.77±0.07	162	0.292	1.975
Zn	32.87±1.10	24.67±1.41	178	4.591	1.973
Mn	767.96±45.35	903.69±38.84	178	2.273	1.973
Cd	0.62±0.08	0.77±0.06	178	1.416	1.973
Cr	3.21±0.23	2.62±0.16	158	2.076	1.975
water					
Pb	0.02±0.00	0.02±0.00	178	0.770	1.973
Ni	0.03±0.00	0.02±0.00	178	1.307	1.973
Mn	0.74±0.03	0.64±0.03	178	2.672	1.973
Zn	0.02±0.00	0.16±0.00	89	3.311	1.987
Cd	0.004±0.000	0.002±0.000	158	4.389	1.975
Cr	0.020±0.007	0.001±0.000	89	2.649	1.987

Zn in fish significantly ($P<0.05$) varied seasonally and was high during the wet season which could be attributed to the high concentration in water. Similar results where Zn significantly differed seasonally ($P<0.05$) were recorded from Ikpoba river with 0.02±0.01 during the dry season and 2.05±0.15mg/kg during the wet season (Oguzie and Izevbigie, 2009).

Mn, Cr, Pb and Zn in sediment significantly varied seasonally ($P<0.05$) with Mn and Pb being high during the wet season while Zn and Cr were high during the dry season. Mn, Cr, Cd and Zn in water significantly varied seasonally ($P<0.05$) with Mn, Cd and Cr being high during the dry season and Zn during the wet season. The higher levels observed in the dry season could be due to low volume of water which leads to elemental concentration while the lower levels observed could be attributed to the influx of water from surface runoffs which is capable of washing away some of the heavy metals, thereby reducing their levels (Ideriah *et al*., 2005; Agatha, 2011; Prabal *et al*., 2011).

4.7: Transfer factor (TF) of the studied heavy metals during dry and wet seasons

Seasonal TF of various metals was also calculated between seasonal concentration in fish and water and the values are as presented in Table 4.9.

Table 4.9: Heavy metal transfer factor (TF) in water during the dry and wet seasons

Metal	Period	Station 1	Station 3	Station 7	Station 10
		Transfer Factor			
Pb	Wet Season	108.13	130.00	367.78	277.14
	Dry Season	53.44	284.00	640.00	420.00
Ni	Wet Season	37.22	70.00	17.06	37.73
	Dry Season	21.75	67.50	29.00	6.67
Mn	Wet Season	178.95	218.90	266.30	158.53
	Dry Season	87.82	249.38	134.42	232.72
Zn	Wet Season	396.67	1363.04	710.00	99.53
	Dry Season	3093.75	1000.00	672.73	2800.00
Cd	Wet Season	645.00	-	960.00	-
	Dry Season	304.00	1230.00	355.00	1770.00
Cr	Wet Season	6.67	20.00	-	20.00
	Dry Season	1.03	5.00	6.67	-

The results showed that the TF of all elements in fish from water was greater than one except Cr in sampling station 7 during wet season, sampling station 10 during dry season and Cd in the sampling stations 3 and 10 during wet season. This means that the fish undergo bioaccumulation of these elements from the river water (Rashed, 2001; Authman and Abbas, 2007).

Transfer factors of heavy metals in sediments for dry and wet seasons were determined and the results are recorded in Table 4.10.

Table 4.10: Heavy metals' TF in sediments during the dry and wet seasons

Metal	Period	Station 1	Station 3	Station 7	Station 10
		Transfer Factor			
Pb	Dry Season	0.06	0.05	0.18	0.09
	Wet Season	0.03	0.06	0.07	0.07
Ni	Dry season	0.95	0.89	1.00	0.13
	Wet Season	0.75	7.95	0.13	0.6
Mn	Dry Season	0.08	0.14	0.20	0.36
	Wet Season	0.12	0.19	0.25	0.16
Zn	Dry Season	2.02	0.75	1.06	1.35
	Wet Season	4.44	5.36	1.46	2.60
Cd	Dry Season	2.71	0.95	3.94	35.40
	Wet Season	1.93	2.12	1.39	3.33
Cr	Dry Season	0.10	0.02	0.01	0.00
	Wet Season	0.01	0.02	0.01	0.02

The results showed that the TF of all elements in all the sampling stations are less than one except that of Cd, Ni and Zn. This means that fish least likely get the heavy metal bioaccumulation from sediments. In general the transfer factors of water are greater than those of sediments and most transfer factors from sediments were less than one showing that fish bioaccumulate these elements from water than is from sediments (Rashed, 2001). These results might be due to feeding behaviour of fish (Ali and Fishar, 2005; Abdel-Baki *et al.*, 2011).

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

i. The samples of tilapia fish gills obtained from Mbagathi and Ruiru tributaries during the wet and dry seasons were found to contain all the analysed heavy metals (Pb, Ni, Mn, Zn, Cd and Cr) at different levels.

ii. Concentrations of Ni, Mn and Pb in fish, Pb and Cd in samples of sediments and Pb and Mn in water samples obtained from Mbagathi and Ruiru tributaries during the wet and dry seasons were found to have exceeded the WHO recommended limits.

iii. Samples of sediments recorded the highest concentrations of heavy metals for both dry and wet season as compared to tilapia fish gills and water samples with water samples recording the lowest concentrations.

iv. Water was also found to contain different levels of the heavy metals. The mean levels of Mn were higher than those of the other elements in the samples of tilapia fish gills obtained from Mbagathi and Ruiru tributaries.

v. Mean levels of Pband Cd featured in fish, sediments and water samples with concentrations above the recommended limits by WHO while Cr recorded the lowest concentrations.

5.2 Recommendations

5.2.1 Recommendations from this study

i) There is need for constant monitoring of the trace metal concentrations in Athi River selected tributaries since the river serves as source of drinking water, irrigation and fish for the local inhabitants in the study area.

ii) Riverine vegetation is also recommended along the river for heavy metal absorption from the water and sediments.

5.2.2 Recommendation for further study

1. Since the study dealt with only one part of fish organ, it is therefore recommended that further study be carried out to look into other parts like muscles, kidney, liver and scales as there might exist some differences.
2. Other types of fish like mud fish should be analised for heavy metals to check the level of pollution.
3. Concentration of other heavy metals like mercury, arsenic,copper, iron and others that were not studied should be need be assessed.
4. As the metal concentrations in water are affected by diversified factors such as pH, water temperature, conductivity and organic matter contents need to be investigated.
5. Athi River selected tributaries were found to be polluted, and therefore there is need to do speciation studies of the elements in order to establish the form in which they exist.

REFERENCES

Abdel-Baki, A.S., Dkhil, M.A. and Al-Quraishy, S.1.(2011) Bioaccumulation of some heavy metals in tilapia fish relevant to their concentration in water and sediment of WadiHanifah, Saudi Arabia.*African Journal of Biotechnology*,**10:**2541-2547.

Aceto, M., Abollino, O., Bruzzoniti, M.C., Mentasti, E., Sarzanini, C., Malandrino, M. (2002) *Food Additives and Contaminants*, **19**:126.

Agatha, A.N. (2010) Levels of Some Heavy Metals in Tissues of Bonga Fish, *Ethmallosafimbriata*from Forcados River.*Journal of Applied Environmental and Biological Sciences*,**1:**44-47.

Agency for Toxic Substances and Disease Registry (ATSDR),(2002) Toxicological profile for Manganese and Lead *(Draft for Public Comment).* Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service. http://www.atsdr.cdc.gov/toxprofiles. Accessed on 02/12/2012.

Agency for toxic substances and disease registry (ATSDR) (2005) Toxicologycal profile for lead, cadmium, nickel. Atlanta, U.S. Department of Public Health and Services, Public Health Service.http://www.atsdr.cdc.gov/toxprofiles. Accessed on 08/12/2012.

Ahmad, M.K., Islam, S., Rahman, S., Haque, M. and Islam, M.M. (2009) Heavy metals in water and some fishes of Buriganga River, Bangladesh. *International Journal of Environmental Research*, **4**:321-332.

Ahmed, M.K., Ahamed, S., Rahman, S., Haque, M. R. and Islam, M. M. (2009b) Heavy metal concentrations in water, sediments and their bio-accumulations in fishes and oyster in Dhaleswari River.*Terrestial and Aquatic Environmental Toxicology*, **3**:33-41.

Akan, J. C., Abdulrahman, F.I., Sodipo, O.A. and Akandu, P.I. (2009) Bioaccumulation of some heavy metals of six fresh water Fishes caught from Lake Chad in Doron buhari, Maiduguri, Borno state, Nigeria, *Journal of applied sciences in environmental sanitation*, **4**:103-114.

Alaa, G.M., Osman, W.K. (2010) Water Quality and heavy metal monitoring in water, sediments, and tissues of the African catfish *Clariasgariepinus* (Burchell, 1822) from the River Nile, Egypt. *Journal of Environmental Protection*, **1**:389-400.

Alam, A.M.S., Islam, M.A., Rahman, M.A., Siddique, M.N. and Matin, M.A. (2003) Comparative study of the toxic metals and non-metal status in the major river system of Bangladesh.*Dhaka University Journal* of *Science*, **51:**201-208.

Ali, M.H.H. and Fisher, M.R.A. (2005) Accumulation of trace metals in some benthic invertebrates and fish species relevant to their concentration in water and sediment of Lake Quaran, Egypt, Egyptian.*Journal of Aquatic Research,* **31**:290-30.

Anim, A.K., Ahialey, E.K., Duodu, G.O., Ackah, M. and Bentil, N.O. (2010) Accumulation profile of heavy metals in fish samples from Nsawam, along the Densu River, Ghana. *Research Journal of Environmental and Earth Sciences*,**3**:56-60.

APHA., Eaton, A.D., Mary, A. and Franson, H. (2005) Standard Methods for the Examination of Water and Wastewater. American Water Works Association.

Ashraf, W. (2006) Levels of selected heavy metals in tuna fish.*Arabian Journal Science and Engineering*, **31:**89-92.

Authman, M. and Abbas, H. (2007) Accumulation and distribution of copper and zincin both water and some vital tissues of two fish species (tilapia zilii and Mugilcephalus) of Lake Qarun, Fayoum province, Egypt.*Pakistan Journal of Biological Science,***10:**13.

Awofolu, O.R., Mbolekwa, V.M. and Fatoki, O.S. (2005) Levels of trace metals in water and sediment fromTyume River and its effects on an irrigated farmland 87-94.http://www.wrc.org.za accessed on. 12/11/2012.

Begüm, A., Amin, M.d.N., Kaneco, S. and Ohta, K. (2005) Selected elemental composition of the muscle tissue of three species of fish, *Tilapia nilotica*, *Cirrhinamrigala*and *Clariusbatrachus*, from the fresh water Dhanmondi Lake in Bangladesh. *Food Chemistry*, **93:**439-443.

Bingol, D. and Akcay, M. (2005) Determination of trace elements in fly ash samples by AAS after applying different digestion procedure. *Journal of Quantitative Spectroscopy and Radiative Transfer,* **101:**146-150.

Bury, N.R., Walker, P.A and Glover, C.N. (2003) Nutritive metal uptake in teleost fish. *Journal of Experimental Biology*, **206**:11-23.

Canlý, M. and Atlý, G. (2003) The relationships between heavy metal (Cd, Cr, Cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species. *Environmental Pollution*, **121:**129-136.

Censi, P., Spoto, S.E., Saiano, F., Sprovieri, M., Mazzola, S., Nardone, G., Di Geronimo, S.I., Punturo, R. and Ottonello, D. (2006) Heavy metals in coastal water systems.A case study from the northwestern Gulf of Thailand.*Chemosphere*, **64:**1167-1176.

Christian, G.D. (2005) Analytical Chemistry. 6th Ed John Wiley and Sons. pp 474-478.

Daniel, M.W. and Bhagwan, S.C. (2011) Concentration levels of essential and non-essential elements in selected Ethiopian wines. *Chemical Society of Ethiopia,* **25**:169-180.

Davis, J.R. (2000) Uses of Nickel. ASM Specialty Handbook: Nickel, Cobalt, and Their Alloys. *American Society for Metals International,* 7-13.

Dayan, A.D. and Paine, A.J. (2001) Mechanisms of chromium toxicity, carcinogenicity and allergenicity: Review of the literature from 1985 to 2000. *Human and Experimental Toxicology,* **20**:439-451.

Duan, T., Kang, J., Chen, H. and Zeng, X. (2003) Determination of ultra trace concentration of elements in high purity tellurium by inductively coupled plasma spectrometry after iron(III) hydroxide co precipitation. *Journal of spectrochemica acta part B,***58**:1679-1685.

Ekeanyanwu, C.R., Ogbuinyi C.A. and Etienajirhevwe, O. F. (2011) Trace Metals Distribution in Fish Tissues, Bottom Sediments and Water from Okumeshi River in Delta State, Nigeria.*Environmental Research Journal***, 5**:6-10.

Emsley, J. (2001) Chromium. Nature's Building Blocks.*An A-Z Guide to the Elements*, Oxford, England, UK: Oxford University Press, 495-498.

Emsley, J. (2001) Manganese. Nature's Building Blocks.*An A-Z Guide to the Elements*, Oxford, UK: Oxford University Press, 249-253.

Emsley, J. (2001) Zinc. Nature's Building Blocks.An A-Z Guide to the Elements, Oxford, England, UK: Oxford University Press, 499-505.

Eser, K., Asuman, D., Saraymen, R. and Engin, K. (2004) Comparative quantitative analysis of zinc, magnesium and copper content in the scalp hair of healthy people and breast cancer patients. *Journal of Trace Elements in Experimental Medicine,* **17**:175-180.

FAO, (2003) Committee for Inland Fisheries of Africa.Report of the third session of the Working Party on Pollution and Fisheries. Accra, Ghana.*Food and agricultural Organization, Fisheries Report*, **471:**25-29.

FAO/WHO. (2011) Joint FAO/WHO food standards programme CODEX Committee on Contaminants in Foods. Fifth Session, The Hague, The Netherlands, 14-88.

FAO/WHO. (1984) List of maximum levels recommended for contaminants by the Joint FAO/WHO. *Codex Alimentarius Commission*,**3**:1-8.

Farkas, A. (2000) Heavy Metal Concentrations in Fish of Lake Bolton (Hungary). *Lakes and Reservoirs: Research and Management***, 5:**271-279.

Fatoki, O.S. and Awofolu, O.R. (2003) Levels of Cd, Hg and Zn in some surface waters from the Eastern Cape Province, SouthAfrica.*Water South Africa,* **29:**375-380.

Fernandes, C., Fontainhas-Fernandes, A., Peixoto, F. and Salgado, M.A. (2007) Bioaccumulation of heavy metals in *Liza saliens*from the Esomriz-Paramos coastal lagoon, Portugal.*Ecotoxcolog of Environ and Safety*, **66**:426-431.

Fernandes, C., Fontaínhas-Fernandes, A., Cabral, D. and Salgado, M. A. (2008) Heavy metals in water, sediment and tassues of *Liza Saliens* from Esmoriz–Paramos lagoon, Portugal.*Environmental Monitory Assess*, **136:**267-275.

Food and Agriculture Organisation of the United Nations/ Would Health Organization (FAO/WHO), (2011) Joint FAO/WHO Food Standards Program, CODEX Committee on contaminants in Foods.CODEX AlimmentariuS Commission. pp 1-88.

García, R. and A. P. Báez (2012) Atomic Absorption Spectrometry (AAS), Atomic Absorption Spectroscopy, Muhammad Akhyar Farrukh (Ed.), http://www.intechopen.com/books/atomic-absorption-spectroscopy/atomic-absorption-spectrometry-aas-.Accessed on 19th December 2012.

Zhang, W. and Cheng, C. Y. (2007) Manganese metallurgy review. Part I: Leaching of ores/secondary materials and recovery of electrolytic/chemical manganese dioxide. *Hydrometallurgy***89**: 137–159.

Gonzalez, A. R., Ndung'u, K and Flegal, A.R. (2005) Natural Occurrence of HexavalentChromium in the Aromas Red Sands Aquifer, California.*Environmental Science and Technology* **39**:5505–5511.

Gupta, A., Rai, D.K., Pandey, R.S. and Sharma, B. (2009) Analysis of some heavy metals in the riverine water, sediments and fish from river Ganges at Allahabad. *Environmental Monitoring Assessment*, **157**: 449-458.

Hingston, J. (2001) Leaching of chromated copper arsenate wood preservatives.A *review. Environmental Pollution*, **111**:53-66.

Housecroft, C.E. and Sharpe, A.G. (2008) Inorganic Chemistry (3rd Edition).Prentice Hall.

Ibrahim, S. and Tayel, I. (2005) Effect of Heavy Metals on Gills of Tilapia Ziilli Inhabiting the River Nile Water (Damietta Branch and El-Rahawey Drain), Egypt. *Journal of Aquatic Biology and Fish*, **9**:111-128.

Ideriah, T.J.K., Braide, S.A. and Briggs, A.O. (2005) Distribution of lead and total hydrocarbon in tissues of periwinkles *(Tympanotonousfuscatus*and *Pachymeliniaaurita)* in the upper Bonny River, Nigeria. *Journal of Applied Science and Environmental Management*, **10920**:145-150.

Johnson, A.R., Munoz, A., Gottlieb, J.L. and Jarrard, D.F. (2007) High dose zinc increases hospital admissions due to genitourinary complications. *TheJournal of Urology*, **177**:639-43.

Kage, F.G. (2003) Impact of heavy metal pollution on the composition and abundance of benthic microinvertebrates along Nairobi River, Kenya.Thesis, Kenyatta University.

Kar, D., Sur, P., Mandal, S.K., Saha, T. and Kole, R.K. (2008) Assessment of heavy metal pollution in surface water. *International Journal of Environmental Science and Technology,* **5**:119-124.

Karin, K. and Terry, B. (2004) Sources of Lead Exposure and Intellectual Impairment in Children.*Environmental Health Perspective*, **112**:987-993.

Kasprzak, Sunderman, Jr, F.W. and Salnikow, K. (2003) Nickel carcinogenesis.*Mutation research,* **533**:67-97.

Kithiia, S.M. (2006) The effects of land use types on hydrology and water quality of Upper Athi River basin, Kenya. University of Nairobi.

Lars, J. (2003) Hazards of heavy metal contamination.*British Medical Bulletin,***68**:167-182

Linnik, P.M. and Zubenko, I.B. (2000) Role of bottom sediments in the secondary pollution of aquatic environments by heavy metal compounds.*Lakes and Reservoirs: Research Management,***5**:11-21.

Linnila, P.M. (2000) Zinc, Lead and Cadmium Speciation in Deeper Water Bodies.*Lakes and Reservoirs: Research and Management*,**5**:261-270.

MacFarlane, G.B. and Burchettt, M.D. (2000) Cellular distribution of Cu, Pb, and Zn in the Grey Mangrove Avicemnia marina (Forsk.).*Vierh Aquatic Botanic*, **68:**45-59.

Miller, J.R., Allan, R. and Horowitz, A.J. (2002) Metal Mining in the Environment, Special Issue. *The Journal of Geochemistry: Exploration, Environment, Analysis*, **2**:225-233.

Moore and Attar (2011) Anthropogenic sources of heavy metals in deposited sediments from runoff and industrial effluents, Shiraz, SW Iran**.** *International Conference on Environmental Science and Technology,* **2**:215-219.

Mtanga, A. and Machiwa, J.F. (2007) Heavy metal pollution levels in water and oysters, *Saccostreacucullata*, from Mzinga Creek and RasDege mangrove ecosystems, Tanzania. Africa. *Journal of Aquatic Science,* **32**:235-244.

Mwegoha W. J. S.and Kihampa, C. (2010) Heavy metal contamination in agricultural soils and water in Dar es Salaam city, Tanzania. *African Journal of Environmental Science and Technology,* **4**:763-769.

Muwanga, A. and Barifaijo, E. (2006) Impact of industrial activities on heavy metal Loading and their physico-chemical effects on Wetlands of Lake Victoria basin (Uganda). *African Journal of Science and Technology*,**7**:51-63.

Navin, I., Soylak, M., Elci, L. and Dogan, M. (2000) Determination of trace metal ions by AAS in natural water samples after preconcentration of pyro catechol violet complexes on an activated carbon column. *Journal of Hazardous Materials*,**52**:1041-1046.

Nussey, G., Van Vuren, J.H.J., Du Preez, H.H. (2000) Bioaccumulation of Chromium, Manganese, Nickel and Lead in the tissues of the Moggel, *Labeoumbratus*(Cyprinidae), from Witbank Dam, Mpumalanga. *Water South Africa*, **26**:269-284.

Obasohan E. E. (2008) The use of heavy metals load as an indicator of the suitability of the water and fish of Ibiekuma stream for domestic and consumption purposes. *Bioscience Research Communications*,**20**:265-270.

Obasohan, E.E, Oronsaye, J.A.O. (2004) Bioaccumulation of Heavy metals by some Cichlids from Ogba River, Benin City, Nigeria. *Nigerian Annals of Natural Sciences*, **5**:11-27.

Obasohan, E.E. (2008) Heavy metals concentrations in the offal, gill, muscleand liver of a freshwater mudfish (*Parachannaobscura*) from Ogba River, Benin city, Nigeria.*African Journal of Biotechnology*,**6**:2620-2627.

Oguzie, F.A. and Izevbigie, E.E. (2009) Heavy metals concentration in the organs of the silver Catfish, *Chrysichthysnigrodigitatus*(Lacèpéde) caught upstream of the Ikpoba river and the reservoir in Benin City. *Bioscience Research Communications*, **21**:189-197.

Oguzie, F.A. (2003) Heavy metals in Fish, Water and Effluents of lower Ikpoba River in Benin City, Nigeria.*Pakistan Journal of Science and Industrial Research*, **46**:156-160.

Oronsaye, J.A.O., Wangboje, O.M. and Oguzie, F.A. (2010) Trace metals in some benthic fishes of the Ikpobariver dam, Benin City, Nigeria;*African Journal of Biotechnology*,**9**: 8860-8864.

Öztürk, M., Özözen, G., Minareci, O.and Minareci, E. (2009) Determination of heavy metals in fish, water and sediments of avsar dam lake in turkey.*Iranian Journal of Environmental Health Science and Engineering**6:***73-80.

Prabal, B., Abhijit, M., Kakoli, B.andChowdhury, M.S.N. (2011) Seasonal Variation of Heavy Metals Accumulation in Water and Oyster (*Saccostreacucullata*) Inhabiting Central and Western Sector of Indian Sundarbans.*Environmental Research Journal*, **5**:121-130.

Rashed, M.N. (2001) Monitoring of environmental heavy metals in fish from Nasser lake.*Environment International*, **27:**27-33.

Reilly, C. (2002) Metal contamination of food. Backwell Science Limited. USA, 81-194.

Safty, A.E., Khalid, E., Mahgoub, S.H. and Neveen, A.M. (2008) Zinc toxicity among galvanization workers in the iron and steel industry.*Annals of the New York Academy of Sciences,* **1140**:256-262.

Salnikow, K. andDenkhaus, E. (2002) Nickel Essentiality, Toxicity, And Carcinogenicity. *Critical Reviews in Oncology/Haematol,* **42**:35-56.

Samir, M.S. and Shaker, I.M. (2008) Assessment of heavy metals pollution in water and sediments and their effect on oreochromis niloticus in the northern delta lakes, Egypt. *International Symposium on Tilapia in Aquaculture,* **8**:475-490.

Skoog, D.A., West, D.M., Holler, F.J. and Crouch, S.R.(2005) Fundamentals of Analytical Chemistry. Publisher, Chemistry: David Harries, 8th Ed, pp 720-723.

Storelli, M.M., Storelli, A., D'ddabbo, R., Marano, C., Bruno, R., Marcotrigiano, G.O. (2005) Trace elements in loggerhead turtles (*Carettacaretta*) from the eastern Mediterranean Sea: Overview and evaluation. *Environmental Pollution,* **135:**163-170.

Tawari-Fufeyin, P. and Ekaye, S. (2007) Fish Species Diversity as Indicator of Pollution in Ikpoba River, Benin City, Nigeria.*Reviews in Fish Biology and Fisheries,* **17**:21-30.

Teugels, G.G. and D.F.E. Thys van den Audenaerde, (2003) Cichlidae. The fresh and brackish water fishes of West Africa. Paris, France.

Türkmen, M. and Ciminli, C. (2007) Determination of metals in fish and mussel species by Inductively Coupled Plasma-atomic emission spectrometry. *Food Chemistry,* **103:**670-675.

Tüzen, M. (2003) Determination of heavy metals in fish samples of the MidDamLake Black Sea (Turkey) by graphite furnace atomic absorption spectrometry. *Food Chemistry,* **80:**19-123.

Wachira, D.N. (2007) Physico-electrochemical assessment of pollutants in Nairobi river.Thesis, University of Nairobi.

World Health Organization, (2000) Hazardous Chemical in Human and Environmental Health. W.H.O. Geneva. Switzerland.

World Health Organisation (WHO) (2008) Guidelines for Drinking-water Quality; 3rd Edition 1-459.

World Health Organization WHO (2003) Chromium , zinc, lead, in drinking-water. *Background document for preparation of WHO Guidelines for drinking-water quality,* Geneva, (WHO/SDE/WSH/03.04/4).

APPENDIX I

Calibration Curves for the used standards

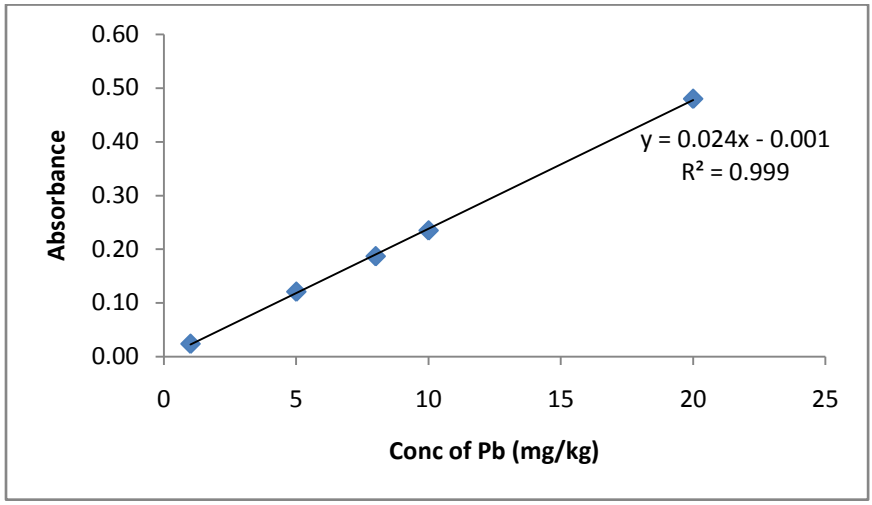

Figure 35.2.1 Calibration curve for Pb

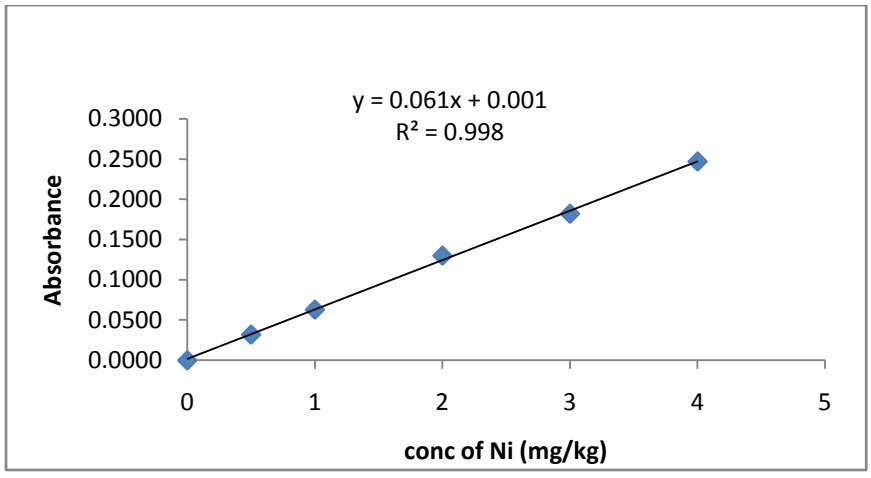

Figure 45.2.2: Calibration curve for Nickel

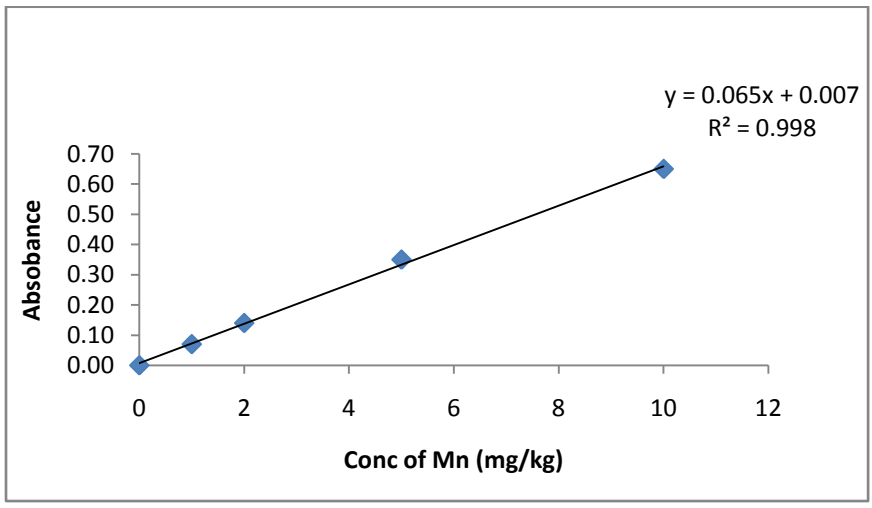

Figure 5.2.3: Calibration curve for Mn

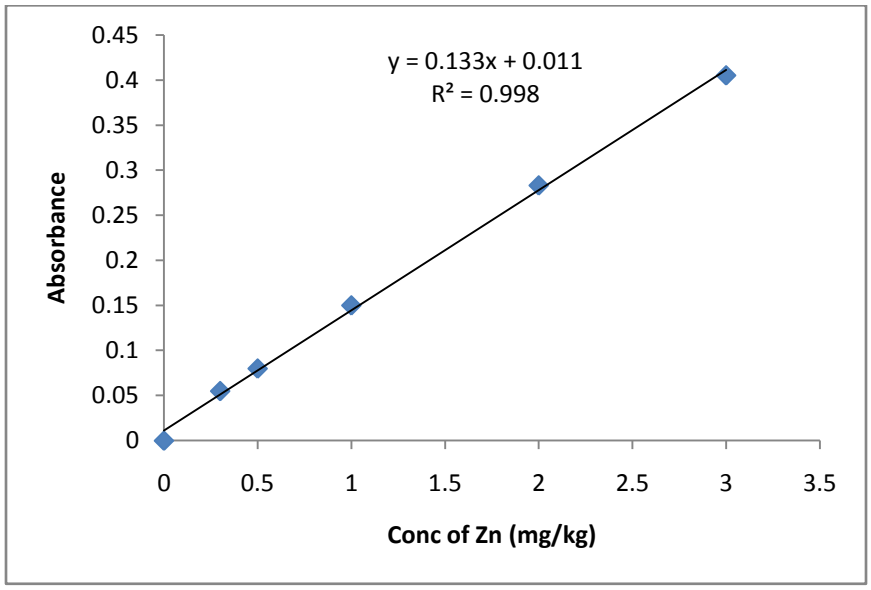

Figure 65.2.4: Calibration Curve for Zn

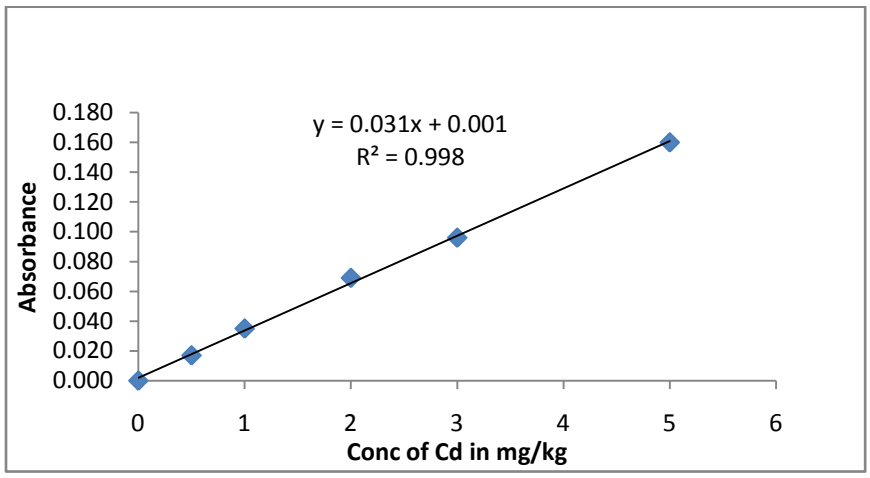

Figure 5.2.5Calibration curve for Cd

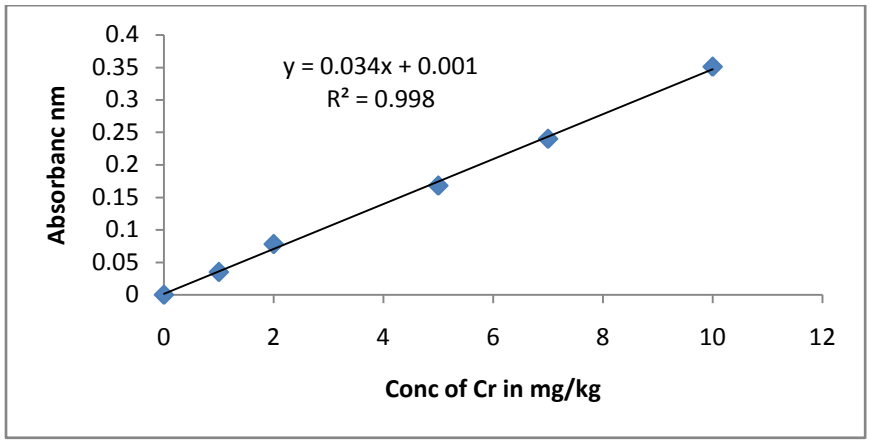

Figure 75.2.6: Calibration curve for Cr

APPENDIX II

Dry	wPb	wCd	wNi	wZn	SMn	SCr	SPb	SCd	SNi	SZn	FCd	FZn
wMn	0.113	0.122	0.041	**0.277**	-0.015	-0.144	**-0.221**	**-0.240**	-0.140	-0.178	-0.094	0.145
wCr	**0.684**	**0.595**	**0.365**	0.094	**0.343**	**-0.277**	0.080	0.197	**0.396**	**-0.326**	**0.440**	0.151
wPb	1	**0.703**	**0.484**	0.118	**0.402**	-0.154	0.075	**0.262**	**0.307**	**-0.371**	0.287	0.162
wCd		1	**0.296**	**0.268**	**0.408**	-0.178	-0.017	**0.227**	**0.288**	**-0.375**	0.033	-0.018
wNi			1	0.033	0.140	-0.047	0.007	0.079	**0.332**	-0.178	0.244	0.182
wZn				1	0.202	-0.124	0.059	-0.010	0.015	0.044	**-0.436**	-0.092
SMn					1	0.099	**0.486**	**0.407**	0.000	0.172	0.138	-0.023
SCr						1	0.167	0.122	**-0.300**	**0.414**	0.261	-0.013
SPb							1	**0.571**	-0.068	**0.699**	0.131	0.049
SCd								1	-0.098	**0.284**	0.123	0.324
SNi									1	**-0.273**	0.184	-0.219
FPb											**-0.629**	-0.089
FNi												**0.546**
FZn												1

Table 5.1: Correlation Analysis of metals during dry season

*bold values are significant at 95% confidence level ($p<0.05$).S-sediment, F-fish W-water.

Table 5.2: Correlation Analysis of metals during wet season

Wet	wMn	wCd	wZn	SMn	SCr	SPb	SCd	SNi	SZn	FCr	FCd
wMn	1	0.081	**0.488**	0.136	-0.050	0.106	0.083	**-0.265**	**-0.668**	**-0.433**	-0.215
wCr		0.155	0.196	**0.281**	0.122	0.182	0.046	0.019	-0.081	0.107	0.119
wPb		**0.239**	0.072	-0.127	-0.151	-0.070	0.173	-0.073	0.079	0.234	0.138
wCd		1	-0.139	**0.341**	0.110	**0.350**	-0.189	-0.165	0.021	-0.084	0.061
wNi			**-0.383**	-0.024	-0.062	0.018	0.049	0.074	0.157	0.400	-0.003
wZn			1	**0.273**	0.183	0.165	**0.222**	-0.004	**-0.418**	-0.158	-0.067
SMn				1	**0.277**	**0.553**	-0.028	-0.061	**-0.209**	0.070	-0.144
SCr					1	**0.564**	**0.295**	**0.360**	0.159	0.057	-0.158
SNi								1	**0.308**	**0.442**	0.078
SZn									1	0.238	-0.167
FMn										0.009	-0.366
FCr										1	0.177
FPb											**-0.625**
FCd											1

*Bold values are significantly higher at 95% confidence level($p<0.05$).S-sediment, F-fish W-water.

APPENDIX III

Photograph of Tilapia fish and the fish gills

Figure 85.2.7: Tilapia Fish

Figure 95.2.8: Tilapia Fish gills