# SELECTED HEAVY METALS IN WATER AND SEDIMENTS AND THEIR BIOCONCENTRATIONS IN PLANT *(Polygonum pulchrum)* IN SOSIANI RIVER, UASIN GISHU COUNTY, KENYA

**BY**

**JUDITH JEPKOECH**

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# DECLARATION

## DECLARATION BY CANDIDATE

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**Judith Jepkoech** (SES/PGH/07/08) **Date**

## DECLARATION BY SUPERVISORS

This thesis has been submitted with our approval as University supervisors.

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**Dr. G.M. Simiyu** **Date**

Department of Environmental Biology and Health

School of Environmental Studies

University of Eldoret

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**Dr. M.K. Arusei** **Date**

Department of Chemistry and Biochemistry

School of Science

University of Eldoret

# DEDICATION

To my most beloved parents

# ABSTRACT

The study was aimed to measure total concentrations of heavy metals lead, zinc and copper in water, sediment and plants samples and to assess heavy metals bioconcentration factors in plant (*Polygonum pulchrum*) in Sosiani River, located in Uasin Gishu County in Kenya. Sampling was done for six months between January 2010 and July 2010. Water, sediment and plant samples were collected from sampling points selected along Sosiani River extending from Naiberi to Huruma downstream using stratified sampling technique. The sediment and plant samples were dried in the oven at 50°C to constant weight and digested in a mixture of acids according to standard procedures. The water samples, digests of sediments and plants were analysed for heavy metals using Atomic Absorption Spectrophotometer (model AAS Variant 200). The results showed that the highest total heavy metals concentration in water were Cu (0.18±0.04 ppm); Pb (0.46±0.09 ppm) and Zn (0.70±0.22 ppm) at sites Kapsabet_Eldoret Bridge, MTRH and West Indies respectively. Highest recorded sediment total heavy metals were Cu (1.62±0.14 ppm); Pb (1.27±0.17 ppm) and Zn (6.73±0.88 ppm) at sites market, MTRH and Islamic Center respectively. Fractionation of heavy metals in sediments showed low percentage solubility (Cu 9.3%; Pb 8.5%; Zn 4.2%). Concentration of zinc in studied plants was highest (3.60±0.63 ppm) at Kapsabet-Eldoret Bridge, with bioconcentration factor of 15.1 times based on soluble zinc fraction and lowest at Huruma with a bioconcentation factor of 7.9. This indicates that conditions in the study area show preferential zinc metal uptake in plants compared to Cu and Pb. This may pose Zn metals health risks due to accumulation along the food chain. Suggestions are made for monitoring of heavy metals bioaccumulation in organisms such as fish in the study area.

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# DEFINITION OF TERMS AND ABBREVIATION

**Bioavailability: -** It’s the way chemicals are absorbed by organisms. Its also the degree to which a chemical becomes available to the target tissue after administration.

**Bioaccumulation**: - An increase in the concentration of a chemical over time in a biological organism compared to the chemical’s concentration in the environment.

**Bioconcentration**: - Specific bioaccumulation process by which the concentration of a chemical in an organism becomes higher than it’s concentration in the environment around the organism.

**Bioconcentration factor**:-refers to the ratio of a contaminant of potential concern concentration in aquatic organism eg plant, fish to the concentration of the surrounding water.

**Toxicity**: - the capacity of a substance to cause injury to a living organism

**FAO**: - Food and Agricultural Organization.

**WHO**: - World Health Organization

**MTRH -** Moi Teaching and Referral Hospital

# CHAPTER ONE

## 1.0 INTRODUCTION

### 1.1 Background of the Study

Water is essential to life since it is a part of every cell and it assists most basic functions like respiration and digestion. Water is also a good solvent and many substances, some useful and some harmful to life may be dissolved in it. Because of the importance of water, the pattern of human settlement throughout history has often been determined by its availability (Dobson and Burges, 2007). With growth, demand for water has increased dramatically, and its uses have become much more varied as used in agriculture, industry, recreation, and non-ingested personal consumption. Frequently, each of these uses requires a different level of quality in order for the water to be considered adequate.

Besides being vital, water is also considered to be a limited resource; population growth, industrial developments and other pressures faced by developing countries have lead to structured measures to ensure sustainable management of this important source (Dobson and Burgess, 2007). Many heavy metals and their compounds that may be found in water have been found to be toxic and undergo biomagnifications (Karvelas *et al*., 2003).

Water is exposed to various natural and/or anthropogenic influences in the form of pollutants, for example, sodium chloride, toxic metals such as lead, cadmium and chromium. Other pollutants include pathogens such as bacteria and viruses (Ali, 1999). These could be harmful to the humans when high concentrations are found in water.

Rivers are a dominant pathway for metals transport (Miller *et al.,* 2003) and trace metals may become significant pollutants of many small riverine systems. The behaviour of metals in natural waters is a function of the substrate sediment composition, the suspended sediment composition, and the water chemistry (Osmond *et al.,* 1995). During their transport, the trace metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena (Dassenakis *et al.*, 1997; Akcay *et al.*, 2003) which affect their bioavailability (Nicolau *et al.*, 2006). Contamination of rivers with heavy metals may cause devastating effects on the ecological balance of the aquatic environment and the diversity of the aquatic organisms (Suziki *et al.,* 1988)

The effect of a pollutant on a target organism may either be lethal or sub-lethal (Manson, 1991). Lethal effects occur quickly and death is usually the criterion, while sub-lethal concentration of toxic pollutants may affect the behavior of organisms that may lead to reduction in the fitness of the natural population.

In many cases, heavy metals occur in natural bodies of water at levels below their toxic thresholds. However, due to their non-degradable nature, they accumulate in the environment and pose risk of damage via uptake and subsequent bioaccumulation by organisms. Several scientific observations have shown that heavy metals are bioconcentrated or bioaccumulated in one or several compartments across food webs (Bryan and Langston, 1992; Kiffney and Clement, 1993; Oyewo, 1998, Otitoloju and

Don-Pedro, 2003). Metal bioaccumulation can be of importance from the public health point of view, especially for human at the end of the food chain.

Secondly, the phenomenon of bioaccumulation of heavy metals is now being exploited in the assessment of environmental quality, in addition to chemical surveys of water and sediment. The inclusion of bioaccumulators in a biological monitoring programme is particularly advantageous since such organisms are known to accumulate these pollutants to levels several folds higher than the amount in the external medium, demonstrating how biological systems can render unsafe, the otherwise low and apparently safe prevalent ambient levels of persistent pollutants in ecosystems (Otitoloju and Don-Pedro, 2004).

The problems of indiscriminate use of chemicals in the agricultural fields, industries, factories ultimately drains into adjacent water bodies and carried downstream through the river waters.

Humans have always depended on aquatic resources for food, medicines and materials as well as recreational and commercial purposes such as fishing and tourism. In addition, aquatic ecosystems have significant impact on migratory bird species that use the water bodies as sanctuary and stop-over for food, breeding and nesting.

The urban aquatic ecosystems are strongly influenced by long term discharge of untreated domestic and industrial wastewaters, storm water runoff, accidental spills and direct solid waste dumping (Sarika, 2008). All these released pollutants have a great ecological impact on the water quality and its surrounding food web (Hejabi, 2009). Sediments are integral and inseparable parts of the aquatic environments because they help to determine the overall assessment of heavy metals in water visa-avis aquatic life and their survival. Since sediments play a very important role in physicochemical and ecological dynamics, any change in toxic concentrations of heavy metal residues on the sediments will affect the natural aquatic life support systems.

The increasing pollution of rivers connected with disposal of wastes originating in industrial emissions and in industrial, agricultural and household uses of water is well known. Experts estimate that wastewater fed directly into water bodies may introduce as many as a million different pollutants into our aquatic ecosystems. Moreover, major factors for sensitivity of aquatic ecosystems to pollution, besides role of these systems as receiving bodies for effluents, may be related with structure of food chain.

An important link in the transfer of heavy metals from soil/sediment to man is plants. Element content of essential elements in plants is conditional, the content being affected by the geochemical characteristics of a soil and by the ability of plants to selectively accumulate some of these elements. Bioavailability of the elements depends on the form of their bond with the constituents of a soil. Plants readily assimilate through the roots such compounds, which dissolve in waters and occur in ionic forms. Additional sources of these elements for plants are: rainfall; atmospheric dusts; plant protection agents; and fertilizers, which could be absorbed through the leaf blades (Lozak *et al.*, 2001).

Among animal species, fishes are the inhabitants that cannot escape from the detrimental effects of these pollutants (Olaifa *et al.,* 2004). Fish are widely used to evaluate the health of aquatic ecosystems because pollutants build up in the food chain and are responsible for adverse effects and death in the aquatic systems (Farkas *et al.,* 2002). The studies carried out on various fishes have shown that heavy metals may alter the physiological activities and biochemical parameters both in tissues and in blood (Basa and Rani, 2003). The toxic effects of heavy metals have been reviewed, including bioaccumulation (Waqar 2006). The organisms developed a protective defense against the deleterious effects of essential and inessential heavy metals and other xenobiotics that produce degenerative changes like oxidative stress in the body (EL-Naga *et al.*, 2005).

The distribution of heavy metals in sediments can provide evidence of the anthropogenic impact on aquatic ecosystems and therefore aid in assessing the risks associated with discharged waste. River bed sediments act as both carriers and source of contamination in an aquatic environment; not only play an important role in river water pollution but can also provide a record of river's pollution history (Tsai *et al.*, 2003). To assess the environmental impact of polluted sediments, information on total metal concentrations alone is not sufficient as heavy metals are present in different chemical forms in sediments (e.g. metal carbonates, oxides, sulfides, organometallic compounds, etc.) (Stecko and Bendell-Young, 2000; Bendell-Young *et al.,* 2002). Metal fractions can be easily remobilized and hence the chemical form of metals in the sediment is of great significance in determining their remobilization potential (Rauret *et al.,* 1988; López-Gonzáles *et al.,* 2006).

Studies on the distribution and speciation of heavy metals in sediments can provide the actual environmental impact and bioavailability. It has generally been accepted that the most appropriate methods to evaluate solid speciation-defined as the identification and quantification of the different species, forms or phases present in sediment are selective extraction procedures (Kot and Namiesnik, 2000; Ramirez *et al*., 2005). Selective extractions are widely used in sediment analysis to evaluate long-term potential emission of pollutants and to study the distribution of pollutants among the geochemical phases (Rauret, 1998), and to determine the metals associated with source constituents in sedimentary deposits (Van der Sloot *et al.*, 1997).

Eldoret town is one of the growing towns in Kenya, which is drained by River Sosiani. Sosiani River drains agricultural farmlands and Eldoret municipality that is rapidly industrializing. Application of fertilizers and other pesticides lead to input of heavy metals in the catchments which may find their way into the river through runoff. Industries and municipal treatment plant discharge effluents to the river adding heavy metal burden to the water. Once in the river, fluctuations of water parameters such as salinity and pH usually render these metals somewhat bioavailable and they ultimately bioaccumulate in the organisms.

Heavy metals such as cadmium, chromium, copper, iron, lead, manganese and zinc are environmentally harmful substances, and this necessitates their surveillance in aquatic environments. Low concentrations of heavy metals occur in natural aquatic ecosystems, but recent expansions in human population growth, industry, and peri-urban agricultural activities have led to an increase in heavy metal occurrence in excess of natural levels (Biney *et al.*, 1994).

The aim of this study is to assess the relationship between metal concentration (lead, zinc, and copper) in Water, Sediment and plant (Polyonum pulchrum) of River Sosiani and Sediment fractionation.

## 1.2 Statement of the Problem

Heavy metals in aquatic environment are currently a major concern worldwide and ranked as a major polluting chemicals in both developed and developing countries (Lloyd, 1992) due to their toxicity and threat to plant and animal life as they cause environmental contamination. Increasing population trends and up-coming industries in the close vicinity of water bodies pose problems to the quality water. Many people depend on this water for domestic uses and for irrigation, while others could be sourcing their protein like fish from the river. The accumulations of pollutants pose a great risk, not only to aquatic organisms but also humans along the food chain due to bioaccumulation. Sosiani River drains agricultural and urban centers in Uasin Gishu County and may be polluted with toxic heavy metals. The various forms of the metals could be bio-available in levels that are harmful to life forms. The potential or extent of health risks has not been documented. This study aims at assessing potential risks posed by the heavy metal species in River Sosiani.

## 1.3 Overall Objective of the Study

The overall goal of this study was to assess bioconcentration of heavy metals zinc, copper and lead in plant (*Polygonum pulchrum)* in River Sosiani within Eldoret Municipality.

## 1.4 Specific Objectives.

i. To measure total concentrations of heavy metals lead, zinc and copper in water, Sediment and plants samples from River Sosiani.

ii. To assess the heavy metals fractionation in water and sediments in Sosiani River

iii. To determine the pH in sediments along River Sosiani

iv. To establish the heavy metals bioconcentration factors in plants from River Sosiani

## 1.5 Hypothesis

Ho: Total concentrations of heavy metals in sediments, water and plants found in Sosiani River are not bioavailable.

## 1.6 Significance of the Study

River basin pollution is an aspect of environmental degradation and it requires regular monitoring because its implications on health of aquatic organisms as well as on human health. This information can be used as a foundation for a comprehensive water quality study of the River Sosiani. As part of an effort to continue monitoring the ecological health of River Sosiani, this study is important as it will establish the relationship between metal bioaccumulation in the plant and metal concentration in water and sediments. This is significant to the health organisms in the river and also the public using sosiani river as a source of domestic water.

## 1.7 Study Area

### 1.7.1 Location

River Sosiani is located in the larger Uasin Gishu County. It lies between 0.52 latitude (0°31’ 0N) and longitude 35.28( 35°16’60 E). Altitude ranges from 1500m above sea level at Kipkaren River to 2700m above the sea level at Timboroa (Figure 1).It traverses Eldoret Municipality from Kaptagat. The river is one of the major tributaries of River Nzoia which drains into Lake Victoria.

There are several industries and factories in Eldoret Town such as Kenya Co-operative Creameries Ltd. (KCC), Timber Treatment International (TTI), Corn Products Company (CPC), Ken Knit, Rupa and Raiply. There also exist several hospitals and Jua Kali light industries. Most of these discharge their effluent into the River Sosiani or to Eldoret Municipal Sewage treatment plant system that finally discharges into the river. There are also non-point sources such as storm run-off, garages as well as drainage from paved and non-paved areas and from open fields within the municipality.

### 1.7.2 Climate

The town is situated in an area with highland equatorial climate. The area’s rainfall is evenly distributed. The annual rainfall ranges from 900mm to1200mm. It occurs between the months of March and September, with two distinct peaks in May and August.

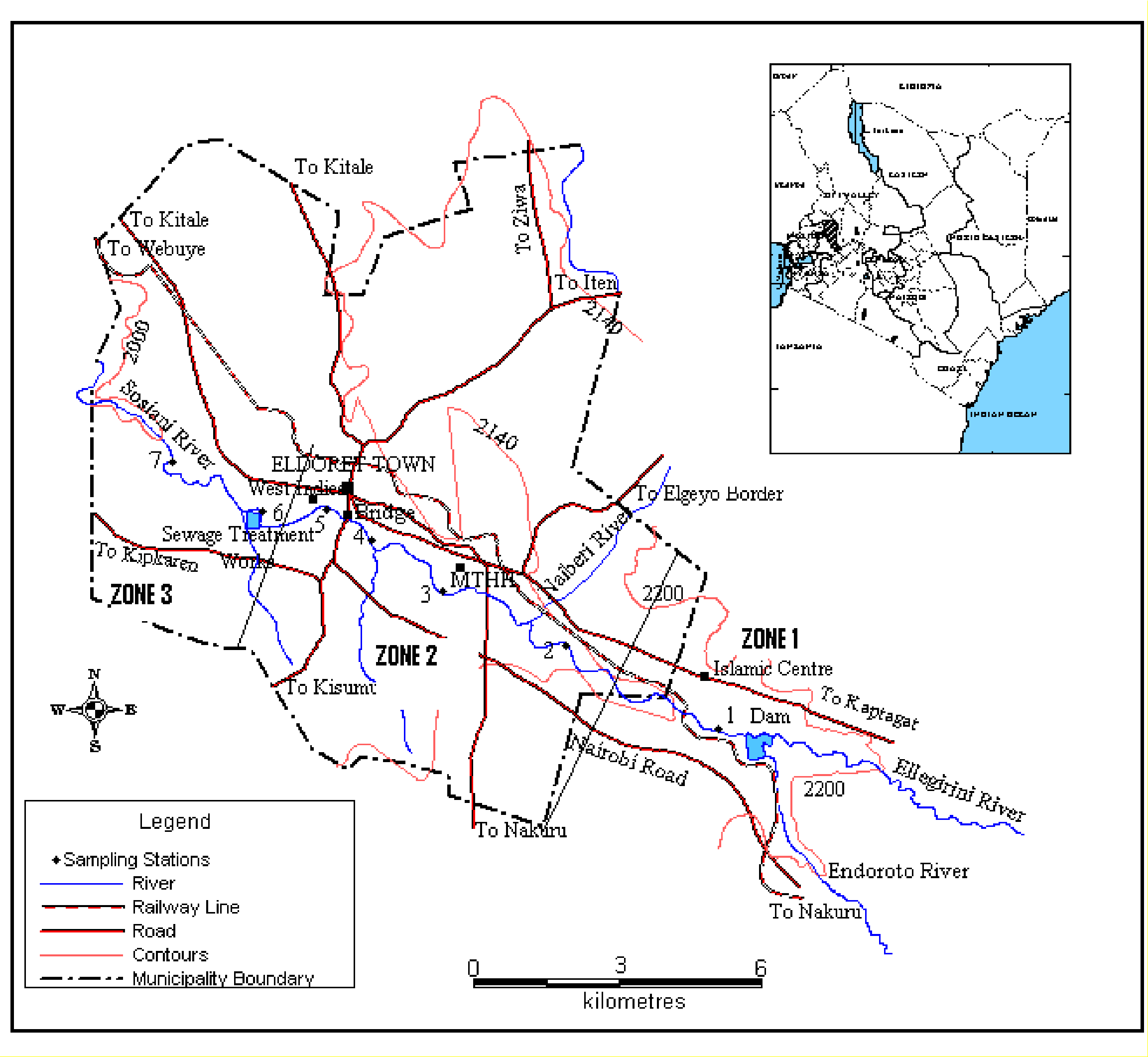

**Figure 1: Zonation and location of study area and sampling sites along Sosiani River.(Zone 1:kaptagat forest, Islamic center where farming activities like wheat and maize and also animal husbandry is carried out; Zone 2:includes central Business District(CBD),garages industries and hospitals like MTRH and Zone 3: estates such as Huruma and sewerage treatment plant.**

**Inset: Location of the study area in Kenya.**

**Source: GIS Lab, Geography Department, Moi University.**

The dry spell begins in November and ends in February. The temperature ranges between $8.4^0$ C and $26.1^0$ C. (District Development Plan, 1999)

### 1.7.3 Land Use and Socio - Economic Activities

The study area is characterized by intense agricultural activities in which chemicals (pesticides, herbicides and fertilizers) are used to control pests, weeds and improve production. Pesticides can reach surface water through runoff from treated plants and soil. Contamination of water by pesticides is widespread. The results of a comprehensive set of studies done by the U.S. Geological Survey (USGS) on major river basins across the country in the early to mid- 90s yielded startling results. More than 90 percent of water and fish samples from all streams contained one, or more often, several pesticides (Kole *et al*; 2001).

The main socio-economic activities include industrial activities and agricultural activities- the latter being practiced in the outskirts of the town. Food crops such as wheat and maize are planted and there is high application of agro-chemicals and fertilizers to improve land productivity and fertility and have environmental consequences. During rainy season they are swept to water bodies through run-offs and end up in River Sosiani, which is main recipient water body. Subsequently, aquatic plants and animals are exposed to these environmental pollution loads.

### 1.7.4 Geology and Soil

The geology of the study area is dominated by tertiary volcanic consisting mainly of basalt rock outcrops of pre-cambian formations. Soils in the area are rich in minerals due to volcanic deposits in the southern two thirds of the district. In its upper course, the river flows through soils developed from intermediate igneous rocks. However, in the lower course, it flows through soils developed from various parent materials. The top layer is mainly red loam soils and underlying is layer of murram. The main soil types are red loam, red clay, brown and brown loam soils (District Development Plan, 1999).

# CHAPTER TWO

## 2.0 LITERATURE REVIEW

### 2.1 Introduction

Heavy metals are those elements whose atomic mass number is more than forty, with density above 4 g/cm$^3$ (Jennett *et al.,* 1980). They occur naturally in the ecosystem with large variation in concentration. Nowadays, however, anthropogenic activities have added a lot of these metals into the environment (Duffus, 2002). Although living organisms including man require varying amount of these metals such as cobalt, iron, copper, manganese, molybdenum and zinc, excessive levels can be damaging to the organisms (Duffus, 2002). Similarly, although many heavy metals are considered as essential macro-elements and micro-elements especially at non-adverse effect levels, they can exert negative effect at concentrations encountered in polluted environment (Dimari *et al.,* 2008). Heavy metals are harmful because they tend to accumulate in the system. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted.

The sources of heavy metals in water may be diverse but are commonly considered as being generally associated with industrial discharges (Agg and Zabel, 1987). Effects of various toxicants will not only depend on the concentration in water or on the form which they take (ionic, complexed, organic) or even on the species of organisms affected, but also will depend on the condition and quality of water itself and on the number ,type and concentration of other toxicants present. The effect of two or more toxicants can be additive, antagonistic or it may be synergistic for example the presence of calcium is antagonistic to the effect of copper, lead or aluminum. Copper behaves synergistically with chlorine, zinc, cadmium and mercury but antagonistically with cyanide (Mason, 1981), Knowledge of the distribution of heavy metals in water, sediment, planktons and fish play a key role in detecting the sources of heavy metal pollution in aquatic ecosystem

### 2.1.1 Copper

Copper is one of the essential elements for the metabolism of many plants and animals. It participates in many enzymatic reactions and is a constituent of the active sites of some enzymes. However, in large quantities copper is toxic. It has a high affinity for organisms and organic matter. A significant portion of the copper present in waters is complexed with organic matter (Leckie *et al.,* 1989). Copper is also removed from aqueous solution by both co-precipitation and absorption during manganese and iron oxide precipitation. It has been reported that most of the copper in the waters is strongly bound on inorganic and organic exchange sites or complexed with organic matter in sediments (Yertushenko et al, 1990; Kosalwat *et al.,* 1987).

### 2.1.2 Zinc

Zinc is a biologically essential nutritional trace element in minute quantities, which is ever present in plants, micro-organisms and animals (Hilmy *et al.,* 1987). Zinc is a common constituent of a variety of industrial effluents (Brungs, 1969; Hellawell, 1986) which is often discharged into aquatic systems and therefore poses a threat to aquatic life. Zinc toxicity is modified by water chemical factors including dissolve oxygen concentration, hardness, pH and temperature of water (Nussey, 1998; Skidmer, 1964). Zinc exists in oxidation state (II) which it is amphoteric. The treatment of waste water in sewage plants leads to the precipitation of zinc. The toxicity of zinc to plants in general is low and is only observed in soils with excessive zinc burden. The signs of zinc in plants are most well described (Merian, 1991).

### 2.1.3 Lead

Lead sources include pipes, battery cases, paints and tetra-ethyl lead (petrol additive). The adverse physiological effects of lead accumulation include damage to the nervous systems, muscular paralysis anemia and liver and kidney damage. Concentrations higher than 0.33 mg/1 damage both fish populations and their food. In contaminated aquatic systems, almost all the lead is tightly bound to sediment. Only a minor fraction is dissolved in the water (Manahan, 1993).

The lead uptake by fish reaches equilibrium only after a number of weeks of exposure. Lead is accumulated mostly in gills, liver, kidney and bone WHO (1989). Ndagijimana (1999) reported that the mean concentrations of lead in river Sosiani ranges between 0.07 to 0.10 ppm and 0.92ppm and 5.60ppm in water and sediments respectively which was higher than the WHO (1998).

## 2.2 Bioavailability of Heavy Metals

The discharge of heavy metals is of major concern because of their toxicity and threat to human life and the environment (Ianni *et al.,* 2003). Heavy metals in contrast with most other pollutants are non-biodegradable and undergo a global ecobiological cycle in which natural waters are the main pathways (Bradshaw, 1992; Welch, 1992).

Although some metals are essential for life, all metals are toxic at high concentrations; for some, for example, selenium, there is narrow window between what is essential and what is toxic. Since many biological systems exist naturally on the margin of metal toxicity, the physical and geochemical redistribution of toxic metals in aquatic environments by human activities has a strong potential to disrupt aquatic ecosystems. However, such disruptions are not determined merely by the quantity of metals redistributed. A number of environmental and biological processes may influence the accessibility of metals to organisms, thus, affecting metal bioavailability (Bernhard *et. al.,* 2001). The possibility that, transformations of waste materials takes place depends upon the chemistry of the material and the action of the environment. Many of these transformations can result in the waste materials being changed to a less toxic form. For example, when chromate wastes are released into the aquatic environment, they are commonly reduced to chromic form, which is more readily bound by the organic and other materials and hence rendered unavailable (Welch, 1992). Also, the oxidation of $SO_2$ to $SO_3$ and again to $SO_4$, was thought to eliminate its toxicity, and was previously used to justify the dispersal of sulphur emissions by tall stacks. This however, failed to take into account the acidifying effects of the sulphate.

Similarly, transformation of waste materials can result in increased toxicity. The most spectacular example of this, is the transformation of mercury compounds (which are not normally poisonous) to methyl mercury, which is extremely poisonous and readily taken up by living organisms (WHO, 1989). This can occur in aquatic systems by biological or chemical processes. The minimata  Bay disease in Japan, caused by the consumption of mercury contaminated fish bears testimony to this phenomenon (Brashaw,1992).Often however, our poor understanding of the processes controlling the biological availability of metals is a major handicap to defining, proving and predicting metal impacts in nature (Aung *et al.*, 2007).

It should be noted that both geochemical and physiological processes are important in determining metal availability. Upon discharge to the aquatic environment, a metal is partitioned between solid and liquid phases, and within each phase, further partitioning or speciation occurs among specific ligands, determined by ligand concentrations and the strength of each metal-ligand association (Nicolau *et al.*, 2006). Thus organism is never exposed to a metal as single entity (Sodre' and Grassi, 2006). Within each phase, the organism is exposed to a variety of physicochemical forms of each metal, and each form often differs in its accessibility to the organism.

In the water phase, the chemical form of a metal determines the biological availability and chemical reactivity (sorption/desorption, precipitation/dissolution) towards other components of the system. This also determines the rate of metal release to the liquid phase and hence the likelihood of remobilization and bioavailability (Bubb and Lester, 1991). Therefore the determination of the total content of heavy metals alone is insufficient in assessing their environmental impact, since it is the chemical form that determines the metal behavior in the environment and their mobilization ability (Ma and Rao, 1997). Hence, it is necessary to assess both total contents of the hazardous substances, as well as the chemical forms in which they may be present (Ma and Rao, 1997).

In an attempt to assess the bioavailability of heavy metals in soils, sediments, sewage sludge and sludge amended soils, several function schemes have been described in the literature (Panda *et al.,* 1995; Mcgrath and Quevanviller, 1996; Ma and Rao, 1997). However, only a few of these procedures were utilized, to the study of distribution of heavy metals in sludge and sludge-amended soils (Dudka and Chlopecka, 1990; Lo and Chen, 1990; Ma and Rao, 1997; Moturi *et al.,* 2004).

These chemicals fractional procedures were promoted to study toxic heavy metals distribution in soils, sludge-amended soils, sediments, dredging materials and sewage sludge, which constitute the reservoir for potential subsequent release of contaminants available for biological uptake. The relative binding strength can be determined with the application of chemical extraction agents, either singly, or in sequence. Sequential attraction is recognized as a useful method for gaining information on the origin, manner of occurrence, bioavailability, mobilization and transport of heavy metals (Subramanian, 1996; Li and Shuman, 1997; Ma and Rao, 1997; Moturi *et al.,* 2004). For instance, high levels of heavy metals in the water-soluble, exchangeable, acid-soluble and easily reducible fractions may indicate pollution from anthropogenic sources, and may pose immediate environmental threats. On the other hand high levels in the more resistant fractions may be a threat after a long period of time. A high bioavailability is linked to high concentrations and bioaccumulation/biomagnification within organisms which may lead to deleterious effects on biodiversity via the inability to secrete physiologically-stored pollutant concentrations, causing toxic effects that could progress through subsequent levels of the food chain (Mountsouris *et al.,* 2002; Caplat *et al.*, 2005).

To assess the environmental impact of polluted sediments of the total trace metal content is not sufficient, because it is the chemical form of the metal in the sediment that determines its behavior in the environment and its mobilization capacity. It is an important issue to consider when assessing possible biological and environmental impacts in terms of metals bioavailability, fate and water quality criteria (Allen and Hansen, 1996). Selective extraction procedures are useful and versatile techniques to investigate on environmental impacts, bioavailability and metal origin in aquatic ecosystems.

Metals in the aquatic environment are distributed as simple inorganic complexes, as complexes with organic matter, and as metals adsorbed on to suspended matter and particulate bound. Among them, the free ions are known to be the most toxic (Aung *et al.,* 2007). The potential toxicity of heavy metals in sediments is largely dependent on its concentration and the chemical form in which the contaminant occurs (Patrick *et al.*, 2001). In addition, the environmental effect of the heavy metals may also be governed by physicochemical and biological conditions that exist in the sediment itself. For example the aqueous concentration of heavy metals in soils and sediments are controlled by the dissolution and precipitation of discrete mineral phases and therefore contaminant uptake by organisms. As well contaminant transport in natural systems is more significant in the solution phase (Traina and Laperche, 1999).This means that the thermodynamic solubility of contaminants containing minerals in the environment can directly influence the chemical reactivity, transport and ecotoxicity of their constituent ions. Factors like low redox potential are one of the major variables that keep metals in non-bioavailable from mainly as refractory sulphides and metal organic complexes (Lacerda *et al.,* 2004).

## 2.3 Heavy Metals in Aquatic Plants

Chemicals derived from agricultural operations (pesticides and herbicides) and industrial effluents, such as metals, ultimately find their way into a variety of different water bodies and can produce a range of toxic effects in aquatic organisms, ranging from alterations to a single cell, up to changes in whole populations (Bernet *et al,*. 2000). The accumulation of toxic metals to hazardous levels in aquatic biota has become a problem of increasing concern. Excessive pollution of surface waters could lead to health hazards in man, either through drinking of water and/or consumption of fish (Mathias, 2001). The increasing importance of fish as a source of protein and the interest in understanding the accumulation of heavy metals at the trophic levels of the food chain, extend the focus towards finfish (Deb, 2003). Pollution enters fish through five main routes: Via food or non-food particles, gills, oral consumption of water and the skin. On absorption, the pollutant is carried in blood stream to either a storage point or to the liver for transformation and/or storage.

Pollutants transformed in the liver may be stored there or excreted in bile or transported to other excretory organs such as gills or kidneys for elimination or stored in fat, which is an extra hepatic tissue (Obasohan, 2007). The concentration of any pollutant in any given tissue therefore depends on its rate of absorption and the dynamic processes associated with its elimination by the fish.

Although zinc and copper have a crucial role in several enzymatic processes, they are tentatively classified as highly toxic metals by Hellawell (2000) and are bioaccumulated in aquatic organisms. Carino and Cruz (1999) suggested that higher concentrations of zinc impair reproductive success and survival potential of *Tilapia nilotica* in zinc-contaminated ecosystems. This heavy metal can exert adverse toxicological effects, when present in high concentrations in water (Pelgrom, *et al.*, 2002). In fact, it is potentially toxic when the internal available concentration exceeds the capacity of physiological detoxification processes. The higher the BCF value the higher the risk posed to the organisms along the food chain. BCF values > 2 were regarded as high values (Mellem *et al.*, 2009).

On the other hand, organs of aquatic animals may accumulate copper when exposed to toxic concentrations (Mazon *et al.*, 2002), which can lead to redox reactions generating free radicals and, therefore, may cause biochemical and morphological alterations (Varanka *et al.*, 2001). In addition, lead residues could result in haematological, gastrointestinal and neurological dysfunction in animals. Severe or prolonged exposure to lead may also cause chronic nephropathy, hypertension and reproductive impairment. Lead inhibits enzymes, alters cellular calcium metabolism and slows nerve conduction.

Heavy metals are accumulated in different components of the environment in different ways being controlled by various mechanisms. Aquatic plants absorb heavy metals from the water; those rooted ones also from the bed material. Generally, aquatic plants can accumulate high amounts of heavy metals. In such a way, they reflect the toxicity of the water environment, and may serve as a tool for the biomonitoring of contaminated waters (Cardwell *et al.,* 2002).

Kumar et al. (2010) in a study on selected metals in sediment, phytoplanktons and fishes of Bindal River Dehradum India, reported that the samples from Bindal River contained metal content higher than WHO standards of 1997. Copper concentrations were 13 µg/l in water, 13µg/l in sediment and 13 µg/l in fish. For lead it was 2.2 µg/l in water, 31 µg/l in sediment,and 10µg/l in phytoplankton and 5.6µg/l in fish. The occurrence of lead concentrates in phytoplankton was attributed higher than water, sediment and fish because it eliminates metals from water, accumulates and stores them over a long period even when concentrations of metals in water are low. This study did not show the origin or the potential sources of the heavy metals.

In this study, an aquatic plant (*Polygonum pulchrum)* was selected according to its availability along the Sosiani River. This plant belongs to the *Polygonaceae* family. A brief description of this plant is it is an herbaceous perennial with stems, found along the rivers. It’s a drought resistant plant thus used to graze animals during dry seasons.

## 2.4 Environmental and Health effects of Heavy Metals

Aquatic organisms may be adversely affected by heavy metals in the environment. Toxicity is largely a function of water chemistry and sediment composition in the surface water system (Pohl *et al.,* 1993). Slightly elevated metal levels in natural waters may cause sub lethal effects in aquatic organisms. Such effects may lead to change in reproduction, the behaviour and morphological changes in tissues. Fresh water fish and invertebrates, aquatic plants are less sensitive to lead and zinc thus the water resource should be managed for protection of fish and invertebrates in order to ensure aquatic plant survivability.

Phytoplanktons and zooplanktons often assimilate available metals quickly because of the high surface area to volume ratio. The ability of fish and invertebrates to absorbed metals highly depends on the physical and chemical characteristics of the metal. Metals may enter the systems of aquatic organisms via three main path ways (HELCOM, 1996)

i. Free metal ions that are adsorbed through respiratory surfaces (for instance gills) are readily diffused into the bloodstream.
ii. Free metal ions that are adsorbed onto surfaces are passively diffused into the blood stream
iii. Metals that are sorbed onto food and particulate matter may be ingested, as well as free ions ingested in water

Ingestion of metals such as lead and copper may pose great risks to human health. Lead, for example, interferes with essential nutrients of similar appearances such as calcium ($Ca^{2+}$) and zinc ($Zn^{2+}$). Because of size and charge similarities; lead can be substituted for calcium and be included in the bones. Children are especially susceptible to lead because developing skeletal systems require high calcium levels. Lead that is stored in bone is less harmful but if high levels of calcium are ingested later, lead in the bones may be replaced by calcium and remobilized into the blood system thereby causing toxicity. Such lead effects may be manifested as nephrotoxicity, neurotoxicity and hypertension. Lead account for most of the cases of pediatric heavy metal poisoning (Reeves et al., 2004).

In humans, exposure to lead may result in a wide range of biological effects depend on the level and duration of exposure. High levels of exposure may result in toxic biochemical effects in humans which in turn cause problem in synthesis of haemoglobin, effects of kidneys, gastrointestinal tract, joints and reproductive system. Some studies suggested that there may be a loss of up to 2 intelligent quotient points for rise in blood lead levels from 10 to 20ug/dl in young children . Average daily lead intake for adults in UK is estimated at 1.6ug from air, 20ug from drinking water and 28ug from food. Lead in air contributes to lead levels in food through deposition of dust and rain containing the metal; on crops and soil (Reeves *et al.,* 2004).

FAO/WHO has set a limit for heavy metal intake based on body weight for an average adult of 60 kilogram body weight. Provisional weekly intake for lead is 214 µg; copper is 3 mg, while zinc is 60 mg (FAO/WHO, 1999).

In a study carried out by Shitshama (1999) on concentration of heavy metals in water , fish and sediment of Winam Gulf, Lake Victoria, Kenya, it was found out that mean lead concentration in waters ranges from 0.45 to 0.12 ppm and cadmium ranges from 0.01 to 0.02ppm. Lead concentrations in sediment ranged from 21.2 and 76.2 ppm and cadmium ranged from 0.4 to2.8 ppm. The study also found that lead concentration in fish ranged from 12.7 to 36.5 ppm. The water metal concentrations were above the recommended values for drinking water (UNEP/WHO, 1988). The study did not however show the source of heavy metals and their fractionations.

# CHAPTER THREE

## 3.0 METHODOLOGY

## 3.1 Materials and Methods

## 3.2 Study Area.

The study commenced in October 2009 by carrying out a reconnaissance survey of the study area by identifying and selecting sampling stations. Sampling was done for six months (January 2010-June 2010) and this covered wet and dry season, stratified Random sampling was used whereby the river was divided into three zones based on intensity of socio-economic activities (Figure 1). These are the upper part, or peri- urban (zone 1) Naiberi, which is the catchment area consisting of Kaptagat forest, Islamic center where farming activities like wheat and maize and also animal husbandry were carried out, the mid part (zone 2) which include the Central Business District (CBD), road networks, garages and vehicle repair sheds, industries and factories like Ken-Knit, Corn Product Company, Hospitals like Moi Teaching and Refferal Hospital). Finally, was the lower part Zone 3 that is Huruma (covering the area before sewerage treatment and after sewerage treatment).

Naiberi, the first sampling point, was selected in the upper forested part to obtain status of water quality from relatively undisturbed area of the river. The second sampling point, Islamic center; here there are intense agricultural activities including large scale wheat and maize farming as well as animal husbandry. The third sampling station was selected just after Moi Teaching and Referral Hospital, upstream the bridge to capture effects from the hospital and its environs.

The fourth sampling station was at the Kapsabet - Eldoret Bridge where there are a lot of activities taking place like the garages, road networks, CBD, industries and car wash. The fifth sampling station was adjacent to the municipal market; here there are food kiosks, garbage heaps, next to the river bank and garages.

The sampling station six was located at West Indies. This part of the river is wide and fishing activities are carried out. There are also residential houses hence the river is likely to be polluted by domestic waste. Huruma, after the sewerage treatment plant was designated sampling station point seven.

### 3.2.1 Chemicals, Reagents, Materials and Equipments

The reagents consisted of concentrated nitric acid ($HNO_3$) (Analar, England), Hydrogen peroxide ($H_2O_2$) - 30% (reagent grade, Mumbai, India), concentrated Hydrochloric acid (HCl ) (Analar, MERCK Darmstadt, Germany). Others were concentrated sulphuric acid (Analar, MERCK Darmstadt, Germany), distilled water, and standard solution. Materials consisted of Filter papers (Whatman No.42), beakers, conical flasks, volumetric flask, thermometer, pH meter, trowel, polythene bags, ice bags, centrifuge, pestle and mortar, weighing machine and atomic absorption spectrometer (AAS Variant 200).

## 3.3 Field Sampling

### 3.3.1 Water Sampling

Approximately 500 ml of Water was collected at the identified sampling sites using pre-cleaned 0.5 L plastic bottles that had been thoroughly washed and rinsed with distilled water after soaking overnight in dilute nitric acid. During sampling, the bottles were rinsed 3 times with river water before the samples were collected. The water samples were preserved by adding a 2 ml volume of concentrated nitric acid to each sample bottle to prevent precipitation of metals (APHA, 1989). In each case, temperature and pH of water was measured in-situ by use of pH meter model (Jenway 370)

### 3.3.2 Sediment Sampling

One trowel full of deposited layer of Sediment was scooped from same locations as water samples, using a trowel at a depth of 5 cm as this layer takes part in the processes of matter exchange in the rivers. The samples were kept separately in labeled polythene bags placed in ice box and transported to Moi University for treatment and metal analyses

### 3.3.3 Plant Sample

Plant samples were collected as close as possible from same sites as water and sediment samples. The leaves and stem of *Polygonum pulchrum* plant (Appendix 2) were collected and put in polythene bags placed in iced box and then taken to the laboratory for treatment and analysis. *Polygonum pulchrum* plant was found at all sampling stations. The reason for using the plant is drought resistant and the animals feed on it during the dry season.

## 3.4 Laboratory Analysis

### 3.4.1 Heavy Metals in Water Samples

The water sample from each sampling bottle was mixed thoroughly by shaking. A 50 ml aliquot of water sample was pipette into a digestion flask. Digestion was done using a mixture of concentrated nitric acid and sulphuric acid (APHA, 1992). A 3 ml volume of concentrated nitric acid was added and brought to boil slowly on a hot plate controlling the temperature at $70^{0}$C evaporating it to about 15 ml, followed by addition of 3 ml concentrated nitric acid and 5 ml concentrated sulphuric acid while continuing heating until the solution cleared and brown fumes were no longer evident. Digestion was necessary to avoid interferences of complexing organic matter during heavy metal determination. On cooling digested samples were filtered through 0.45um filter paper then topped to the mark with distilled water. The digest was analyzed for total copper, zinc and lead using Atomic Absorption Spectrophotometer (AAS Variant 200).

### 3.4.2 Heavy Metals in Sediment Samples

Sediment samples were first air dried and later oven dried at 50 $^{0}$C for 24 hours to a constant weight. The sediments were crushed with pestle and mortar into fine particles then passed through a 2 mm sieve. A 1.0 g of sieved sample was weight accurately into a digestion conical flask. The sample was refluxed with 5 ml of concentrated nitric acid (analar grade) and shaken for 2 minutes, and then 2 ml of concentrated hydrochloric acid was added while continuing shaking. The Sample mixture was transferred to a hot plate covered with a watch glass. The mixture was heated for about 2 hours until no more brown fumes evolved controlling temperature at 70 $^{0}$C. The solution was cooled, filtered into a 50 ml flask. The filtrate was made to the mark with distilled water. Zinc, copper and in the filtrate were determined using Atomic Absorption Spectrophotometer (Parker, 1972).

### 3.4.3 Heavy Metals in Plant Sample

Plant sample was cleaned with distilled water, air dried and then oven dried to constant weight at 50$^{0}$C. The dried sample was crushed into fine particles in a pestle and mortar and passed through a 2 mm mesh sieve. A 1.0 gram of evenly grounded sample was weighted accurately into a conical flask. A 5ml volume of concentrated sulphuric acid (Analar grade) grade was added. The mixture was gently shaken for 2 minutes, and then slowly 5 ml of 30% hydrogen peroxide was added and left to react. After reaction had subsided the mixture was heated on a hot plate at 70 °C for 2 hours. A 2 ml concentrated nitric acid portion was added to remove excess sulphuric acid. The heating continued until solution of light straw colour was obtained. The solution was cooled, filtered into a

50 ml flask. The filtrate was made to the mark with distilled water. The analysis for heavy metals copper, zinc and lead were done the same way as in case of water samples.

### 3.4.4 Standard Solution Preparation

The heavy metals were determined using the Atomic Absorption spectrometer method. Standard solutions for lead, Zinc and copper were prepared by diluting the stock solution.

#### Lead solutions

#### Lead, Stock Solution Corresponding to 1000mg/l of Pb

Approximately 1.0000gm Pb metal (minimum purity 99.5%) Weighed to the nearest + 0.0002gm, and diluted in a covered 250ml glass beaker with 10ml $HNO_3$ . Then 100ml of water was added. Boil to expel nitrous fumes, cool, transfer to 1000ml volumetric flask and fill to the mark with water.

#### Lead, Standard Solution Corresponding to 10mg/ l of Pb

10.00ml of Pb stock solution was pipetted into a 1000ml volumetric flask. 20ml of nitric acid was added then filled to the mark with water and mix well.

#### Lead, Standard Solution Corresponding to 0.4mg/ l of Pb

20.00ml of Pb standard solution was pipetted into a 500ml volumetric flask.10ml of nitric acid was added and filled to the mark with water and mix well. This solution was prepared on the day of use.

#### Zinc solutions

#### Zinc, Stock Solution Corresponding to 1000mg/l of Zn

Approximately 1.0000gm Zn metal (minimum purity 99.5%) was weigh to the nearest + 0.0002gm, and it was diluted in a covered 250ml glass beaker with 40ml $HNO_3$ . Then

100ml of water was added. Boiled to expel nitrous fumes, cool, transfer to 1000ml volumetric flask and fill to the mark with water.

**Zinc, Standard Solution Corresponding to 10mg/l of Zn**

Pipette 10.00ml of Zn stock solution into a 1000ml volumetric flask. Add 20ml of nitric acid fill to the mark with water and mix well.

**Zn, Standard Solution Corresponding to 0.4mg/l of Zn**

20.00ml of Zn standard solution was pipetted into a 500ml volumetric flask.10ml of nitric acid was added then filled to the mark with water and mix well. This solution was prepared on the day of use.

**Zinc, Standard Solution Corresponding to 0.02mg/l of Zn**

5.00ml of Zn standard solution was pipetted into a 500ml volumetric flask.10ml of nitric acid was added then filled to the mark with water and mix well. This solution was prepared on the day of use.

**Copper solutions**

**Copper, Stock Solution Corresponding to 1000mg/l of Cu**

Approximately 1.0000gm Cu metal (minimum purity 99.5%) was Weighed to the nearest + 0.0002gm, and was diluted in a covered 250ml glass beaker with 10ml $HNO_3$ . Then 100ml of water was added. Boiled to expel nitrous fumes, cool, then transferred to 1000ml a volumetric flask and filled to the mark with water.

**Copper, Standard Solution Corresponding to 10mg/l of Cu**

10.00ml of Cu stock solution was pipetted into a 1000ml volumetric flask. 20ml of nitric acid was added and filled to the mark with water and mix well.

**Copper, Standard Solution Corresponding to 0.4mg/l of Cu**

20.00ml of Cu standard solution was pipetted into a 500ml volumetric flask.10ml of nitric acid was added and filled to the mark with water and mix well. This solution was prepared on the day of use.

Calibration standards were 1ppm, 2ppm and 8ppm for Lead; 0.4ppm, 0.6ppm and 0.8ppm for Zinc, 1.6ppm, 2.4ppm and 3.2ppm for copper. The instrument used for heavy metal analysis was a Varian atomic absorption spectrophotometer (AAS) model 200. The flame gas used as air – acetylene. The concentrations were read directly on the screen. The detection limit of the machine was 0.01ppm for the heavy metal. (APHA, 1992).

### 3.5 Data Analysis

Statistical analysis was done using standard formulas for mean and graphs (Zar, 1984). The students' statistical t-test was used for significant difference at $p=0.05$.Analysis of variance (ANOVA) was done to test for the differences among different means at $p=0.05$. To test for the relationship between pH and concentration of Heavy metals, correlation coefficient analysis was used.

### 3.6 Bioconcentration Factor

Bioconcentration factor (BCF) was used to determine the quantity of heavy metals absorbed by the plant from the sediment. This is an index of the ability of the plant to accumulate a particular metal with respect to its concentration in the soil and is calculated using the formula (Ghosh and Singh, 2005):

Bioconcentration factor (BCF) = (Metal concentration in the whole plant ($C_p$)/Initial concentration of metal in the soil or sediment ($C_s$)

That is BCF = $C_p/C_s$ ---------------------------------------------------------------------- (Eq. 1)

## 3.7 Determination of Heavy Metal Fractionation

The most widely used methods are based on sequential extraction procedures, where several reagents are used consecutively to extract operationally-defined phases from the sediment in a set sequence (Lopez-Sanchez *et al.*, 1993). There are many such schemes (Stover *et al.,* 1976; Tessier *et al.,* 1979; Forstner, 1982) among which the most widely used is the one proposed by Tessier et al. (1979). For the purpose of heavy metal fractionation, two steps were used. These are water soluble and exchangeable fraction.

### i) Water Soluble Fraction

Two grams of wet sediment sample were weight into a 40 ml polycarbonate centrifuge tubes. A30 ml volume deionised-distilled water was added and centrifuged at 10,000 revolutions per minute (rpm) for 2 hours. The supernatant was separated using a pipette, filtered through a 0.2 µm nucleopore polycarbonate membrane filter and analyzed for zinc, lead and copper using an atomic absorption spectrometer (AAS, Variant model 200).

### ii) Exchangeable Fraction

For exchangeable fraction the residue from the water soluble fraction was extracted with 16ml of 1M $MgCl_2$ (adjusted to pH 7.0). The supernatant was separated by centrifuging at 10,000 rpm for 1 hour then filtered through a 0.2 µm nucleopore polycarbonate membrane filter and analyzed for zinc, lead and copper as in (i) above.

# CHAPTER FOUR

## 4.0 RESULTS

## 4.1 Total Heavy Metals Concentrations

### 4.1.1 Copper Concentrations in Samples along River Sosiani

The mean copper concentrations sediments, water and plant (*Polygonum pulchrum*) are summarized in Table 4.1.

**Table 4.1: Total Copper concentrations in samples (mg/kg)**

| | Concentration mg/kg | | | | | |
|---|---|---|---|---|---|---|
| **Station** | **Sediments** | | **Water** | | **Plants** | |
| | Season | | Season | | Season | |
| | **Dry** | **Wet** | **Dry** | **Wet** | **Dry** | **Wet** |
| **Naiberi** | 0.91±0.19[a] | 0.62±0.10[a] | 0.18±0.03[ab] | 0.29±0.40[ab] | 0.44±0.13[a] | 0.69±0.03[a] |
| **Islamic center** | 0.92±0.31[a] | 0.56±0.07[a] | 0.17±0.03[ab] | 0.10±0.03[ab] | 0.20±0.16[a] | 0.66±0.12[a] |
| **MTRH** | 1.62±0.14[a] | 0.68±0.07[a] | 0.18±0.04[ab] | 0.08±0.04[ab] | 0.06±0.04[a] | 0.67±0.06[a] |
| **K-Eld Bridge** | 1.29±0.20[a] | 0.80±0.10[a] | 0.14±0.03[ab] | 0.04±0.04[ab] | 0.16±0.05[a] | 0.60±0.05[a] |
| **Market** | 1.08±0.11[a] | 0.65±0.09[a] | 0.18±0.05[ab] | 0.07±0.06[ab] | 0.32±0.23[a] | 0.60±0.05[a] |
| **W. Indies** | 1.55±0.32[a] | 0.71±0.15[a] | 0.18±0.02[ab] | 0.09±0.04[ab] | 0.47±0.13[a] | 0.66±0.10[a] |
| **Huruma** | 0.51±0.11[a] | 0.45±0.10[a] | 0.15±0.02[ab] | 0.12±0.02[ab] | 0.24±0.14[a] | 0.71±0.07[a] |
| **Mean** | 1.13±0.17 [a] | 0.63±0.02 [a] | 0.17±0.001 [ab] | 0.11±0.025 [ab] | 0.27±0.03 [a] | 0.65±0.006 [a] |

(a) Denotes concentration value significant at 0.05.

(ab) Denotes concentration value insignificant at 0.05.

### *Sediment Copper Concentrations*

With respect to sediment copper concentrations, there was a significant variation in mean copper concentration in sediments between sampling stations between dry and wet seasons (df =1, f = 35.79 $p<0.05$). Copper concentrations were generally higher in dry season as compared to wet season. This may be attributed to lose of water due to evaporation and decrease volume of water. The average concentration of copper in sediments in dry season was at 1.13±0.17mg/kg with an average value of 0.634±0.02 mg/kg being recorded in wet season, giving a range of 0.496 mg/kg. During dry seasons sediments sampled at referral site had the highest concentration at 1.62±0.14 mg/kg followed by West Indies at 1.55 mg/kg with Huruma station contributing the least value at 0.513mg/kg. In wet season bridge sampling site had the highest concentration at 0.79±0.1 mg/kg followed by West Indies at 0.71±0.15 mg/kg with least concentration occurring at Huruma sampling station at 0.456±0.10mg/kg.

### *Water Copper Concentrations*

There was no significant variation in mean copper concentration in water samples among sampling stations in the two seasons of dry and wet seasons (df =1, f = 3.36, $p=0.07$). Copper concentrations in water samples were generally higher in dry season as compared to wet season probably due to dilution by rain water as well as runoff. The mean concentration of copper in sediments in dry season was at 0.17±0.001mg/kg with an average value of 0.11±0.025mg/kg in wet season. In dry season water sampled at Referral site had the highest concentration at 0.18±0.04mg/kg and the least occurred at Bridge at

0.027mg/kg. In wet season West Indies sampling site had the highest concentration at 0.099±0.037mg/kg with least concentration occurring at Huruma sampling station at 0.123±0.021mg/kg. (Table 4. 1)

***Plant Copper Concentrations***

Varied significantly among sampling stations in the two seasons of dry and wet seasons (df =1, f = 102.2, $p<0.05$).Copper concentrations in plant (*Polygonum pulchrum)* samples were generally higher in wet season as compared to dry season. The mean concentration of copper in plant (*Polygonum pulchrum*) in dry season was at 0.27±0.03mg/kg with a mean value of 0.65±0.006mg/kg being recorded in wet season. In dry season plant sampled at West Indies had the highest concentration at 0.465±0.13mg/kg with least occurring at referral at 0.055±0.036 mg/kg. In wet season Huruma sampling site had the highest concentration at 0.71mg/kg with least concentration occurring at Huruma sampling station at 0.596mg/kg. (Table 4.1).

### 4.1.2 Lead Concentrations in Samples along River Sosiani

The mean lead concentrations in sediments, water and plant (*Polygonum pulchrum)* are summarized in Table 4.2.

**Table 4.2 Total Lead Concentrations in Samples (mg/kg)**

| Station | Sediments | | Water | | Plants | |
|---|---|---|---|---|---|---|
| | Season | | Season | | Season | |
| | Dry | Wet | Dry | Wet | Dry | Wet |
| **Naiberi** | 0.98±0.24$^{a}$ | 1.10±0.09$^{a}$ | 0.26±0.01$^{a}$ | 0.18±0.03$^{a}$ | 0.25±0.02$^{a}$ | 0.34±0.06$^{a}$ |
| **Islamic Centre** | 0.63±0.10$^{a}$ | 1.29±0.20$^{a}$ | 0.36±0.05$^{a}$ | 0.17±0.03$^{a}$ | 0.42±0.03$^{a}$ | 0.62±0.19$^{a}$ |
| **MTRH** | 0.63±0.10$^{a}$ | 1.1±0.16$^{a}$ | 0.42±0.07$^{a}$ | 0.18±0.04$^{a}$ | 0.50±0.03$^{a}$ | 0.61±0.07$^{a}$ |
| **K - Eld Bridge** | 0.73±0.07$^{a}$ | 0.83±0.21$^{a}$ | 0.46±0.09$^{a}$ | 0.14±0.03$^{a}$ | 0.51±0.13$^{a}$ | 0.43±0.09$^{a}$ |
| **M. Market** | 1.27±0.17$^{a}$ | 0.75±0.16$^{a}$ | 0.43±0.15$^{a}$ | 0.18±0.05$^{a}$ | 0.59±0.09$^{a}$ | 0.76±0.04$^{a}$ |
| **W. Indies** | 1.04±0.13$^{a}$ | 1.31±0.17$^{a}$ | 0.28±0.14$^{a}$ | 0.18±0.02$^{a}$ | 0.40±0.14$^{a}$ | 0.59±0.05$^{a}$ |
| **Huruma** | 0.67±0.08$^{a}$ | 1.3±0.15$^{a}$ | 0.43±0.11$^{a}$ | 0.15±0.02$^{a}$ | 0.45±0.15$^{a}$ | 0.53±0.04$^{a}$ |
| **Mean** | 0.85±0.07$^{a}$ | 1.09±0.07$^{a}$ | 0.38±0.013$^{a}$ | 0.17±0.001$^{a}$ | 0.44±0.02$^{a}$ | 0.55±0.02$^{a}$ |

(a) Denotes concentration value significant at 0.05.

***Sediments Lead Concentrations***

There was a significant variation in mean lead concentration in sediments between sampling stations in the two seasons of dry and wet seasons (df =1, F = 12.3 $P<0.05$).(Appendix I) Wet season recorded high mean values of lead concentration at 1.099±0.07mg/kg with dry season having mean concentration value at 0.85±0.07mg/kg. In dry season market sampling station had the highest concentration at 1.27±0.17mg/kg with least concentration at Islamic at 0.632±0.1mg/kg. In wet season West Indies had the highest concentration at 1.31±0.17mg/kg with the least at 0.75±0.16mg/kg occurring at market sampling station.

***Water Lead Concentrations***

There was a significant variation in mean lead concentration in water samples among sampling stations and between seasons (df =1, F = 85.4 $P<0.05$) (Appendix 1) respectively. Dry season recorded high mean values of lead concentration at 0.38±0.013mg/kg compared to wet season mean concentration value of 0.17±0.001mg/kg. In dry season Kapsabet - Eldoret bridge sampling station had the highest concentration at 0.46±0.09mg/kg with least concentration at Naiberi at 0.26±0.01mg/kg. In wet season Naiberi had the highest concentration at 0.18±0.03mg/kg with the least at 0.14±0.03mg/kg occurring at bridge sampling station.

### ***Plant Lead Concentration***

There was a significant variation in mean lead concentration in plant (*Polygonum pulchrum)* samples between sampling stations in the two seasons of dry and wet seasons (Df =1, F = 8.16 $P<0.05$). Wet season recorded high mean values of lead concentration at 0.55±0.02mg/kg with dry season having mean concentration value at 0.44±0.02mg/kg. In wet season market sampling station had the highest concentration at 0.76±0.04mg/kg with least concentration at Naiberi at 0.34±0.06mg/kg. In dry season Market had the highest concentration at 0.59±0.09mg/kg with the least at 0.25±0.02mg/kg occurring at Naiberi sampling station.

### 4.1.3 Zinc Concentrations in Samples along River Sosiani

Table 4.3 presents the mean zinc concentrations in water, sediments and plants samples in the study area.

**Table 4.3 Total Zinc Concentrations in Samples**

| | **Concentration in mg/kg** | | | | | |
|---|---|---|---|---|---|---|
| **Station** | **Sediments** | | **Water** | | **Plants** | |
| | Season | | Season | | Season | |
| | **Dry** | **Wet** | **Dry** | **Wet** | **Dry** | **Wet** |
| **Naiberi** | 5.80±0.88$^{ab}$ | 3.69±0.19$^{ab}$ | 0.42±0.20$^{a}$ | 0.33±0.03$^{a}$ | 2.82±0.53$^{ab}$ | 2.81±0.69$^{ab}$ |
| **Islamic** | 6.73±1.11$^{ab}$ | 3.97±0.75$^{ab}$ | 0.31±0.14$^{a}$ | 0.31±0.07$^{a}$ | 1.57±0.99$^{ab}$ | 2.81±0.75$^{ab}$ |
| **MTRH** | 4.21±0.92$^{ab}$ | 5.44±0.30$^{ab}$ | 0.42±0.31$^{a}$ | 0.32±0.04$^{a}$ | 3.3±0.80$^{ab}$ | 2.56±0.60$^{ab}$ |
| **Bridge** | 5.80±0.72$^{ab}$ | 4.75±0.44$^{ab}$ | 0.62±0.26$^{a}$ | 0.35±0.05$^{a}$ | 2.75±0.78$^{ab}$ | 2.99±0.30$^{ab}$ |
| **Market** | 4.40±0.76$^{ab}$ | 5.71±0.61$^{ab}$ | 0.58±0.29$^{a}$ | 0.30±0.08$^{a}$ | 3.60±0.63$^{ab}$ | 1.55±0.32$^{ab}$ |
| **W.Indies** | 3.80±0.42$^{ab}$ | 2.79±0.67$^{ab}$ | 0.70±0.22$^{a}$ | 0.35±0.05$^{a}$ | 2.26±0.09$^{ab}$ | 2.98±0.73$^{ab}$ |
| **Huruma** | 4.23±0.87$^{ab}$ | 3.58±0.28$^{ab}$ | 0.58±0.06$^{a}$ | 0.33±0.05$^{a}$ | 2.3±0.84$^{ab}$ | 1.99±0.35$^{ab}$ |
| **Mean** | 1.13±0.17 $^{ab}$ | 0.63±0.02 $^{ab}$ | 0.17±0.001 $^{a}$ | 0.11±0.025 $^{a}$ | 0.27±0.03 $^{ab}$ | 0.65±0.006 $^{ab}$ |

(a) Denotes concentration value significant at 0.05.

(ab) Denotes concentration value insignificant at 0.05.

***Sediment Zinc Concentration***

There was no significant variation in mean zinc concentration in sediments between sampling stations in the two seasons of dry and wet seasons (Df =1, F = 3.73 P= 0.059) (AppendxI). In Table 4.3 Dry season recorded high mean values of zinc concentration of 6.73±1.11mg/kg at Islamic Center with wet season having mean concentration value at

5.71±0.61mg/kg at the market and 5.44±0.30 at MTRH. In wet season it was lowest at 2.79±0.67mg/kg occurring at West Indies sampling station. The highest level of Heavy metals at Islamic center could be due to farming activities that entails the use pesticides, insecticides and organic fertilizers.

### ***Water Zinc Concentration***

There was significant variation in mean zinc concentration in Water between sampling stations in the two seasons of dry and wet seasons Appendix (Df =1, F = 18.05 P< 0.05). In wet season West Indies sampling station had the highest concentration at 0.67±0.22mg/kg with least concentration at Islamic centre at 0.31±0.04mg/kg .In dry season West Indies had the highest concentration at 0.70±0.22mg/kg with the least at 0.31±0.14mg/kg occurring at Islamic center sampling station.

### ***Plant (Polygonum pulchrum) Zinc Concentration***

There was no significant variation in mean zinc concentration in plant *(Polygonum pulchrum)* between sampling stations in the two seasons of dry and wet seasons (Appendix I) (Df =1, F =0.21 P=0.65. (Table 4.3). In dry season market sampling station recorded highest Zinc concentration at 3.6±0.6mg/kg with least concentration at Islamic at 1.57±0.99mg/kg. In wet season Kapsabet - Eldoret bridge had the highest concentration at 2.99±0.23mg/kg with the least at 1.55±0.32mg/kg occurring at market sampling station.

## Table 4.4 Sediment pH and their Mean Concentrations

| **Sampling site** | **pH** | | **Mean element concentration (ppm)** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Sediment** | **Water** | **Sediment** | | | **Water** | | | **Plant** | | |
| | | | **Cu** | **Pb** | **Zn** | **Cu** | **Pb** | **Zn** | **Cu** | **Pb** | **Zn** |
| Naiberi | 6.91 | 6.9 | 0.67 | 0.90 | 4.34 | 0.23 | 0.26 | 0.37 | 0.56 | 0.29 | 2.81 |
| Is. Center | 5.71 | 6.9 | 0.73 | 0.97 | 5.22 | 0.13 | 0.27 | 0.37 | 0.42 | 0.52 | 2.19 |
| MTRH | 6.89 | 6.8 | 1.14 | 0.87 | 4.82 | 0.13 | 0.29 | 0.37 | 0.36 | 0.55 | 3.03 |
| Kap-Eld B | 7.11 | 6.6 | 1.04 | 0.78 | 5.28 | 0.09 | 0.30 | 0.48 | 0.38 | 0.46 | 2.86 |
| Market | 7.07 | 6.7 | 0.86 | 1.01 | 5.03 | 0.12 | 0.39 | 0.45 | 0.46 | 0.67 | 2.57 |
| W.Indies | 6.76 | 6.8 | 1.13 | 1.18 | 3.29 | 0.14 | 0.23 | 0.51 | 0.56 | 0.49 | 2.74 |
| Huruma | 6.41 | 7.1 | 0.41 | 0.98 | 3.90 | 0.14 | 0.29 | 0.47 | 0.47 | 0.50 | 2.14 |

**Table 4.5: Metal Fractionation in Sediments.**

| Sampling sites | | Copper | | Lead | | Zinc | |
|---|---|---|---|---|---|---|---|
| | pH | Soluble | Exchangeable | Soluble | Exchangeable | Soluble | Exchangeable |
| Naiberi | 6.91 | 0.059(6.8) | 0.052(6.7) | 0.048(4.3) | 0.034(3.0) | 0.191(4.0) | 0.180(3.8) |
| Is Center | 5.71 | 0.056(7.5) | 0.043(3.1) | 0.091(9.4) | 0.022(2.3) | 0.171(3.1) | 0.162(3.0) |
| MTRH | 6.89 | 0.077(6.7) | 0.064(5.6) | 0.024(2.7) | 0.023(2.6) | 0.197(4.0) | 0.011(0.3) |
| Kap-Eld B | 7.11 | 0.098(9.3) | 0.090(8.5) | 0.030(3.8) | 0.028(3.5) | 0.112(2.1) | 0.102(1.9) |
| Market | 7.07 | 0.052(5.9) | 0.049(5.6) | 0.043(4.2) | 0.031(3.1) | 0.212(4.2) | 0.150(2.9) |
| W.Indies | 6.76 | 0.096(8.4) | 0.083(7.3) | 0.043(3.6) | 0.025(2.1) | 0.062(1.8) | 0.082(2.5) |
| Huruma | 6.41 | 0.046(8.4) | 0.013(2.9) | 0.062(6.3) | 0.031(3.2) | 0.182(4.7) | 0.101(2.7) |

NB = The values in brackets shows percentage of elemental concentration to total concentration

## 4.2 pH and Concentrations of Metals in Sediment

Data from this study was statistically analyzed and correlation coefficients illustrating the relationship among plant (*Polygonum pulchrum)*, sediment and pH are shown. The Pearson correlation performed on total concentrations (mg/kg) and the sediment pH (Figure 4.1). Total copper showed a positive correlation (r=+0.491) with the sediment pH. Total Pb, showed positive correlation with all other metals and the pH but showed negative correlation with Zn (r=-0.527).

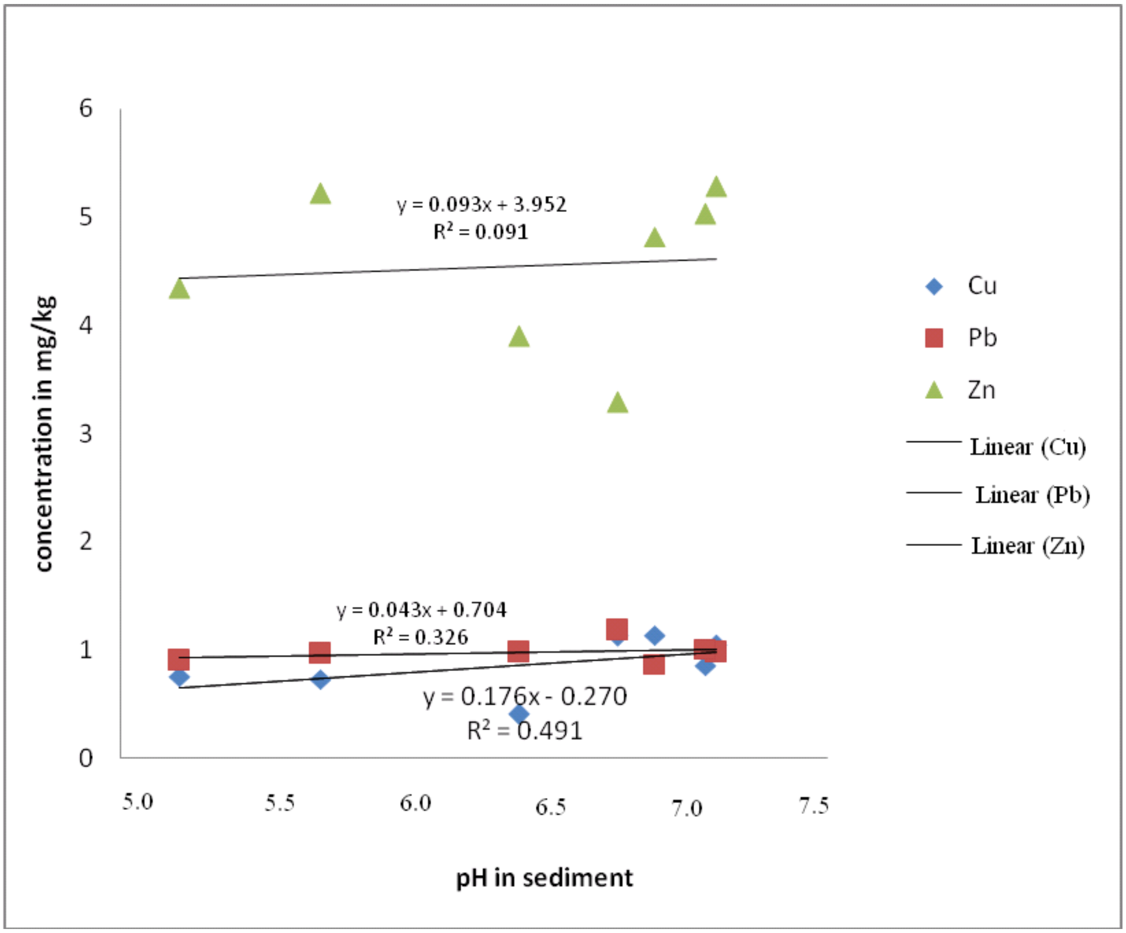

**Figure 4.1** pH in Sediment verses Concentrations of Metals in Sediment

Total Cu showed positive correlation with sediment pH (r=+0.491) (Fig 4.1). Pb was positively correlated with sediment pH (r=+0.424) and positively correlated with cu(r=+0.607). Total Zn was negatively correlated with copper (r=-0.527) at 0.05 level. Zn was positively correlated with sediment pH (r=+0.091), cu (r=+0.079) .

**Table 4.6 Correlations Coefficient Analysis of Total Heavy Metals and pH in Sediment**

| Sediment pH | | | Cu | Pb | Zn | |
|---|---|---|---|---|---|---|
| Sediment pH | Pearson Correlation | 1 | | | | |
| | Sig. (2-tailed) | | | | | |
| Cu | Pearson Correlation | | 0.492 | 1 | | |
| | Sig. (2-tailed) | | 0.263 | | | |
| Pb | Pearson Correlation | | 0.362 | 0.238 | 1 | |
| | Sig. (2-tailed) | | 0.424 | 0.607 | | |
| Zn | Pearson Correlation | | 0.091 | 0.079 | -0.527 | 1 |
| | Sig. (2-tailed) | | 0.846 | 0.866 | 0.224 | |

*Correlation is significant at the 0.05 level (2-tailed). N=7

Figure 4.2 below shows the relationship between pH in sediment and concentrations of heavy metals in the plant. It was observed for both Cu and Pb the relationship was positive, while relationship for Zn was negative ($R^2$= -0.460). The reason for this unexpected relationship could not be immediately established.

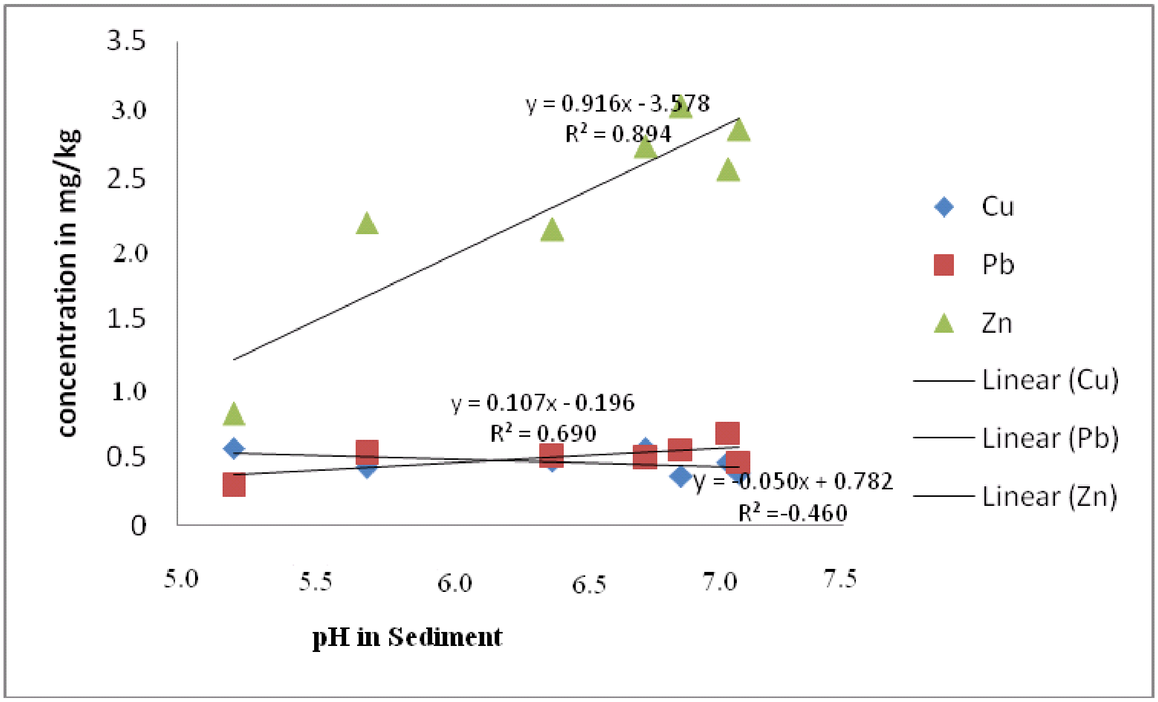

**Figure 4.2 pH in sediment versus concentrations of heavy metals in plants.**

**Table 4.7 Correlations analysis of heavy metals in sediment and plants**

| | | Plant | Cu | Pb | Zn |
|---|---|---|---|---|---|
| Plant | Pearson Correlation | 1 | | | |
| | Sig. (2-tailed) | | | | |
| Cu | Pearson Correlation | -0.460 | 1 | | |
| | Sig. (2-tailed) | 0.299 | | | |
| Pb | Pearson Correlation | 0.690 | -0.453 | 1 | |
| | Sig. (2-tailed) | 0.086 | 0.307 | | |
| Zn | Pearson Correlation | 0.894* | -0.614 | 0.719 | 1 |
| | Sig. (2-tailed) | 0.007 | 0.143 | 0.069 | |

*Correlation is significant at the 0.05 level (2-tailed). N=7

When the water soluble and exchangeable fractions are compared with its total contents, the percentages for each heavy metal varied greatly in the seven sediment samples (Table 4.6). In the sampling site 2, it shows that on average 9.4% of Pb in sediment was associated with water soluble and 2.3% was associated with exchangeable fractions. The percentages of water soluble and the exchangeable fractions were markedly greater than those of Zn (4.0%), (3.8%) and cu (9.1%), (6.7%) respectively. Heavy metals in water soluble and exchangeable fractions are considered more mobile and biotoxic (Gismera, et.al 2004). This suggests that Pb was more mobile to biota.

**Table 4.7 Bioconcentration factors in the samples**

| Sampling stations | Bioconcentration factors | | |
|---|---|---|---|
| | Cu | Pb | Zn |
| Naiberi | 4.8 | 1.9 | 12.4 |
| Islamic centre | 2.4 | 2.4 | 10.2 |
| MTRH | 0.6 | 2.4 | 15.1 |
| Kaps-Eld Bridge | 2.2 | 2.2 | 8.0 |
| Market | 3.6 | 2.6 | 12.4 |
| West Indies | 5.2 | 2.8 | 6.4 |
| Huruma | 2.2 | 2.0 | 7.9 |

As evidence in table 4.7, the BCF ranged from 0.6 (copper) to 15.1 (Zinc) at site MTRH. Zinc with highest BCF showed relatively high positive correlation ($R^2$=0.894) with sediment pH. Figure 4.2 shows that Zinc tended to be available to the plant uptake as the pH increased from acidic to neutral.

# CHAPTER FIVE

## 5.0 DISCUSSION

### 5.1 Total Concentrations of Heavy Metals in Water, Sediment and Plants Samples from River Sosiani

The concentration of heavy metals in water of Sosiani River collected in the dry and wet seasons from the seven sampling sites are given in Table 4.1. Among metals studied in water Zn concentration was highest while Cu concentration was in the lowest. The relatively high zinc at Kapsabet - Eldoret Bridge during the dry season could be due to the discharges of some untreated waste, motor vehicles, some industries and low water level during the dry season. The non point sources of zinc may also find their way into the Sosiani River with the rain water and sewage.

In the sediments the highest (6.73mg/kg) concentration of Zn was found in the Islamic Centre Table 4.3 this could be attributed by the animal husbandry and farming activities around the area as they use pesticides and insecticides. The highest (1.62mg/kg) concentration of Cu was found in Moi Teaching and Referral Hospital (Table 4.1) this could be as a result of the detergents used. At the Municipal Market during the dry season Pb level was highest (Table 4.2) (1.27mg/kg) this could be as a result of metal products, pigments and some chemicals used. The concentrations of heavy metals in plants were higher during the wet season than the dry season. Cu concentration was highest at Huruma (0.71 mg/kg), Pb (0.59mg/kg) at the Municipal Market and Zn (2.99mg/kg) at Kapsabet Eldoret Bridge. Some of the heavy metals levels are far beyond the tolerable level of 0.001µg/g set by WHO (1998).

Muhalulukhu and Tole (2003) observed high levels of lead in their work of analysis of heavy metals in water, fish and sediments of winam gulf. This was attributed to industrial and geological activities in which concentration levels averaged between 0.16-0.94 ppm in water samples and further mean range values of 13-15.8 ppm lead concentrations in fish samples. These values are of human health safety concern as stipulated by WHO(1988) standards which pegs maximum allowable lead levels in human food at 0.05ppm. This work compares well with this study as both concur that these water systems are heavily polluted by lead from mainly industrial, farms and urban associated activities like garages and car wash. Concern arises when the public consumes food like fish from these sources because their health is compromised due to its association with non communicable diseases like cancer.

## 5.2 Bioavailability and Fractionation of Heavy Metals in Sediments

The mean pH and concentration of the sediment samples are summarized in table 4.5. The mean pH varied from 5.21 in the sampling site 1 and 7.11 at sampling site 4. The pH values indicated that the sediments from the study area are slightly acidic. The sediment pH is controlled by the organic matter and anthropogenic activities. The agricultural application of fertilizers, factory effluence, Hospital effluence, domestic and run offs represents a direct input of heavy metals to the sediments altering the pH.

The concentration of heavy metals in sediment was Pb (1.27) at the Market Cu(1.62) at MTRH and Zn (6.73) at Islamic Centre this indicate that a plant can uptake and absorbs higher concentration of Zn than Pb and Cu. This is because of the growth promotry effect of Zn, which acts as plant nutrient and facilitates the plant growth. Increase in pH in sediment increases the metal concentration in plants. Water soluble and exchangeable forms are the most available for plant uptake. Soluble form is not easy available for plant but become mobile and bioavailable under conditions of lower pH.

Sediment contamination poses one of the worst environmental problems in ecosystems, acting as sinks and sources of contaminants in aquatic systems. Sediment analysis plays an important role in assessing the pollution status of the environment (Mucha et al. 2003). Many heavy metals concentrations in sediment, especially in the fine grained sediment, which acts as a transport agent in the water column, are at least three orders of magnitude higher than the same metals in surrounding water. The analysis of heavy metal levels in sediment samples helps in the interpretation of water quality (Heiny & Tate 1997). The heavy metals are present in the river sediments as a result of urban discharge and industrial waste water beside of natural sources. The sediments are also used for determination of heavy metals when the concentrations in water are undetectable with present analyzing methods (Soares et al. 1999).

The bioconcentration factor BF values (Table 4.6) in the studied plant were from 0.6-5.2 in Copper, 1.9-2.8 in Lead and from 8.0 -15.1 in Zinc. The highest bioconcentration factor was at MTRH (15.1) in Zn and Lowest at West Indies at (6.2). The pH plays a critical role in chemistry of river and is an important parameter which affects adsorption of heavy metal on the sediment. A fall in pH may allow realize of toxic metals that would otherwise be absorbs to sediment and essentially removed from the water system. A decrease in pH would increase metal availability lending itself to greater uptake by organisms and can cause physiological damage to life (Connell and Miller 1984). The bioconcentration factors are high at higher pH and this could have been contributed by the anthropogenic activities such as use of organic fertilizers observed in the study area.

# CHAPTER SIX

## 6.0 CONCLUSION AND RECOMMENDATIONS

The study was aimed to measure total concentrations of heavy metals lead, zinc and copper in water, sediment and plants samples. It also aimed at determining pH in sediments along River Sosiani. At the same time heavy metals bioconcentration factors in plants in the study area were assessed.

Based on the results it’s concluded that the total heavy metals studied in water and plant samples are within the accepted limits and others are above the WHO limits. However sediment samples at Islamic center for Zn, Market for Pb and MTRH for Cu were elevated these could be as a result of the activities taking place at those areas like extensive usage agricultural chemicals in the farms, garbage damping along the shores and car washing.

Fractionation of heavy metals in sediments showed low percent solubility (Cu 9.3%; Pb 8.5%; Zn 4.2%). Results showed bioconcentration of heavy metals in studied plants with zinc giving a bioconcentration factor of 15.1 at MTRH which was highest and 6.2 West Indies which was lowest. Zinc is one of the most soluble and mobile metal cations, thus transport from the sediment to roots to shoots of the plants is very high. And because it is easily assimilated by plants, it can be highly phytotoxic (Rout and Das, 2003). The results have indicated the accumulation along the food chain. The mean pH of the sediment from the various sampling sites was slightly acidic and hence tended to influence the uptake of the heavy metals in plants. The bioconcentration factors along Sosiani River are higher and this shows high metals available to the plant hence interfering with the food chain.

The study highlights the significance of the fractionation of metals providing the vital bioavailability. The most mobile heavy metal species occur in fractions I and II, so analysis of the proportions of metals in these fractions provides information on the scale of a potential risk of environment pollution by heavy metals accumulated in the river bottom sediments.

## 6.1 Recommendations

There is a need for controlling point sources that could be contributing to heavy metal pollution along Sosiani River and this could be done by encouraging farmers to use soil and water conservation measures like terracing, growing of cover crops and also Use of organic fertilizer as it does not contain heavy metal.

Continuous monitoring of the river pollution should be carried out and appropriate monitoring protocol be established.

Suggestion is made for further research in monitoring of heavy metal bioaccumulation in organisms such as fish in the study area.

# REFERENCES

Abou EL-Naga, E. H.; EL-Moselhy, K. M.and Hamed, M. A., (2005). Toxicity of Cadmium and Copper and Their Effect on Some Biochemical Parameters of Marine Fish Mugil Seheli. Egyptian. Journal of Aquatic Research, 31 (2), 60-71.

Ademoroti, C.M.A. (1996a). Environmental Chemistry and Toxicology, Foludex Press Ltd., Ibadan, pp. 171–204.

Ademoroti, C.M.A. (1996b). Standard Methods for Water and Effluents Analysis, Foludex Press Ltd., Ibadan, pp. 111– 120.

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. Asian Journal Water Environmental Pollution (in press). Trace metal pollution in coastal areas of Bangladesh. (Proceedings of an International Symposium on ‘Coastal Pollution and Nutrient Cycles’, United Nations University, Tokyo.

Akcay H., Oguz A. and Karapire C., (2003). Study of Heavy Metal Pollution and Speciation In Buyak Menderes And Gediz River Sediments, Water Res, 37, 813-822.

Ali, S. (1999). Greater Khartoum: The Horizontal Expansion and its Impact on the Development of Settlement (in Arabic)

APHA (1989). Methods for Examinations of Water and Waste Water. 17th Ed. Washington D.C American Public Health

APHA (1992). Standard Methods for Examinations of Water and Waste Water. 18th Ed. Washington D.C American Public Health

Basa, Siraj, P. and Usha Rani, A., (2003). Cadmium Induced Antioxidant Defense Mechanism In Freshwater Teleost Oreochromis Mossambicus (Tilapia). Ecotoxicological Environmental Safety, 56 (2), 218 – 221.

Bernhard T., Neff J. (2001). Metals Bioavailability in the Navy’s Tiered Ecological Risk Assessment Process. Naval Facilities Engineering Command. Issue Papers, 1-15, (http://web.ead.anl.gov/ecorisk/issue).

Bernet, D., H. Schmidt, W. Meier, P. Burkhardt-Hol and T. Wahli, (2000). Histopathology In Fish: Proposal for a protocol to assess aquatic pollution. Journal Fish Dis., 22: 25-34.

Biney C, Amazu AT, Calamari D, Kaba N, Mbome IL, Naeve H, Ochumba PBO, Osibanjo O, Radegonde V. and Saad M.( 1994). Review of Heavy Metals in the African Aquatic Environment. Ecotoxicology. Environmental. Safety; 28:134–159.

Bryan G.W. (1976). Some *Effects* Of Heavy Metal Tolerance In Aquatic Organisms. In: Lockwood A.P.M. (ed.) Effects of pollutants on aquatic organisms. Cambridge University Press. Cambridge, England. pp.7

Cardwell, A.J., Hawker, D.W. and Greenway, M. (2002). Metal Accumulation in Aquatic Macrophytes from southeast Queensland, Australia. – Chemosphere 48: 653-663.

Carino, V.S. and Cruz, N.C. (1999). Effects of Low Levels of Zinc on the Ovarian Development Of Tilapia Nilotica Linnaeus. Science Diliman, 3: 34-45. http://journals.upd.edu.ph/index.php/sciencediliman/article/view/287/272

Chopra, A.K. Pathak and G. Prasad (2009).Scenario Of Heavy Metals Contamination in Agricultural Soil and Its Management. *Journal of Applied Nature Science,* 1: 99-108

Dallinger R. (1994). Invertebrate Organisms as Biological Indicators of Heavy Metal Pollution. Applied. Biochemistry Biotechnology; 48:27–31.

Dimari, G. A., Abdulkarim, F. I., Akan, J. C. and Garba, S.T. (2008): Metal concentrations in Tissues of Tilapia *galier, Clarias lazera*, and *Osteoglosidae* Caught from Alau Dam, Maiduguri, Borno State, Nigeria. American Journal of Environmental Sciences. 4: 473 – 379.

Dassenakis M., Scoullos M. and Gaitis A., (1997), Trace Metals Transport and Behaviour in the Mediterranean Estuary of Archeloos River, Marine Pollution Bulletin, 34, 103-111.

Deb, S.C. and Santra,. S. C (2003). Bioaccumulation of Heavy Metals in Fishes. An in-vivo experimental study of sewage-fed ecosystem. Environment, 17: 27-32.

Dirilgen, N. (2001). Accumulation of Heavy Metals in Freshwater Organisms: Assessment of toxic interactions. Turkish Journal Chemistry, 25 (3)**,** 173-179.

Dibson, R.S and Burgess, J.E (2007).Biological Treatment of Precious metal Refinery Wastewater.A Review Mineral Engineering, 20:519-532.

Duffus, J. H. (2002). Heavy metals IUPAC Technical Report. Volume 74. Pp. 793 – 8

El-Khodari, N (2003). The Nile River: Challenges to sustainable development, Presentation to the River Symposium CEO, Nile Basin Society, Canada

Farkas, A., Salanki, J.; Specziar, A., (2002). Relation between Growth and the Heavy Metal Concentration in Organs of bream Abramis brama L. populating lake

Balaton. Arch. Environmental Contamination Toxicology, 43 (2), 236-243.

Farombi, E. O.; Adelowo, O. A. and Ajimoko. Y. R., (2007). Biomarkers Of Oxidative Stress and Heavy Metal Levels As Indicators Of Environmental Pollution In African Cat Fish (*Clarias gariepinus*) from Nigeria Ogun River. *International Journal of Environmental Research Public Health*, 4 (2), 158-165.

Fufeyin, P.T., (1994). Heavy Metal Concentrations in the Water, Sediment and Fish Species of Ikpoba Reservior, Benin City. Ph. D. Thesis, University of Benin, Benin City, Nigeria

Geoffrey. (1990). Pollution Threat of Heavy Metals in Aquatic Environments. Pollution monitoring series. Elsevier applied science

Gosh.M.,and Singh S.P.(2005). A comparative study of Cadmium Phytoextraction by accumulator and weed species. Environmental pollution, 188: 365-371.

Hejabi, A.T. and Belagali S.L. (2009). Survey of Trace Metal Contaminants in Sediments of Kabini River in the Nanjangud industrial area, Mysore District. Nature Environmental Pollution Technology, 8: 49-52.

Hellawell, J.M. Ed., (2000). Biological Indicators of Freshwater Pollution and Environmental Management. Elsevier Applied Science Publishers Ltd., London and New York, ISBN: 10-1851660011, pp: 546.

Hlavay J., Prohaska T., Heiny, J.S. & Tate, C.M. (1997). Concentrations, Distributions and Comparison of Selected Trace Elements in Bed Sediment and Fish Tissue in the South, Platte, River, Basin, USA, 1992–1993. Archives of Environmental Contamination and Toxicology 32: 246–259.

Hossain, M. S. (1996). Progress Report On Bio–Accumulation And Seasonal Variation Of Stress Metals In Water, Sediment And Commercially Important Fishes And Shellfishes Of The North Eastern Bay Of Bengal. Dissertation, University of Chittagong, Bangladesh. 23.

Lakkas TD (Ed*.)*. Heavy Metals in the Environment, CEP Consultants, Edinburgh Vol. 2.

Javed, M. (2003). Relationships among Water, Sediments and Plankton For The Uptake and Accumulation of Metals in the River Ravi. *Industrial Journal Plant Science*, 2: 326–331

Javed, M. and Hayat, S. (1995). Effect of Waste Disposal on the Water Quality of River Ravi From Lahore To Head Baloki. Proc. Pak. Cong. Zoology, 15: 41–51

Khaled A. (2004.) Heavy Metal Concentrations in Certain Tissues of Five Commercially Important Fishes from El-Mex Bay, Al-Exandria, Egypt. pp 1- 11

Kole RK, Banerjee H, Bhattacharyya A.(2001). Monitoring of market fish samples for Endosulfan and Hexachlorocyclohexane residues in and around Calcutta. Bulletine Environmental Contamination Toxicology, 67:554–559. [PubMed]

Koller, K., Brown, T., Spurgeon, A., Levy, L., (2004). Recent Development in Low Level Exposure and Intellectual Impairment in Children. Environmental Health Perspective, 112 (9), 987-994.

Kot, A. and Namiesnuk, J. (2000). The Role of Speciation in Analytical Chemistry, Trace-Trend Analytical Chemistry, 19: 67-79

Larsson A, Haux C, and Sjobeck M. (1985). Fish Physiology and Metal Pollution: Results and Experiences From Laboratory And Field Studies. Ecotoxiclogy Environmental Safety 9: 250- 281.

Lopez-Gonzales, N., Borrego, J., Morales, J.A., Carro, O. and Lozano-Soria (2006). Metal Fractionation in Oxic Sediments of an Estuary Affected By Acid Mine Drainage (South-Western Spain), Estuary Coast. Shelf Science, 08:297-304

Ma J. R, Shao M. H, (1994). Variation in Heavy Metal Pollution of Offshore Sedimentary Cores in Jinzhou Bay. China Environmental Science, 14: 22–29.

Ma J. R, Zhang F. R, Ma D. Y(1989). The Distributive Characteristics of Chemical Speciation of Heavy Metals in the Sediments in Jinzhou Bay. *Journal of Liaoning Normal University,* 1: 48–57

Manahan, S. E. (1993). Environmental Chemistry, 5th Ed., Lewis Publishers, Inc. Michigan.pp 147-150.

Mason,C.E.(1981).Biology Of Freshwater Pollution, Nairobi ,Longman publishers

Mathis, B.J. and T.F. Cummings, (2001). Selected Metals In Sediments, Water And Biota Of The Illinois River. *Journal of Water Poll*ution *Control Tropical,* 45: 1573-1583.

Mazon, A.F., Cerqueira C.C.. and Fernandes M.N, (2002). Gill Cellular Changes Induced By Copper Exposure in the South American Tropical Freshwater Fish Prochilodus Scrofa. Environmental Research, 88: 52-63.

Mellem J., Baijanth H., Odhav B., (2009). Translocation and Accumulation of Cr,Hg, As,Pb,Cu, and Ni by Amaranthus Dubius(amaranthaceae) from contaminated Sites. Journal of Environmental Science and Health, 44:568-575.

Miller C.V., Foster G.D. and Majedi B.F., (2003), Baseflow And Stormflow Metal Fluxes From Two Small Agricultural Catchments In The Coastal Plain Of Chesapeake Bay Basin, United States, Applied Geochemistry, 18, 483-501.

Mucha, A.P., Vasconcelos, M.T.S. & Bordalo, A.A. 2003). Macro benthic community in the Douro Estuary: relations with heavy metals and natural sediment characteristics. Environmental Pollution 121: 169–180.

Morgan, J.J. and Stumm, W. (1991). Chemical Processes In the Environment, Relevance of Chemical Speciation, In: Merien, E. (ed.), Metals and Their Compounds in the Environment, pp: 67–103. VCH Publishers, Germany

Mountsouris, A., Voutsas, E. and Tassios, D. (2002) Bioconcentration of heavy metals in aquatic environments: the importance of bioavailability. Marine Pollution Bulletin, **44**, 1136-1141.

Ndagijimana.A, (1998). The Impacts Of Eldoret Municipal And Industrial Effluents On River Sosiani:Ecological and Public Health Aspects. M.phil thesis pg 87, SES Moi University,Eldoret,Kenya

National Environmental Management Council (NEMC) (1994).Report Of Nation Environmental Management Council And Working Groups On Monitoring Of Mercury And Other Heavy Metals Pollution In Gold Mining Areas Around L.Victoria, Tanzania.

Nicolau, R, Galera-cunha,A. and Lucas,Y. (2006). Transfer of Nutrients and Labile Nutrients from the continent to the sea by small Mediterranean River.Chemosphere 63:469-476.

Nairobi River Basin Programme (NRBP)-Phase II (2003). Pollution Monitoring and Sub-Component. Final Report University of Nairobi

Nussey,G. (1998) Metal Ecotoxicology Of The Upper Olifants River At Selected Localities And The Effect Of Copper and Zinc On Fish Blood Physiology. Physiological response of tilapia, *Orechromis mossambicus*, to sublethal copper

Obasohan, E.E., (2007). Heavy Metals Concentrations in the Offal, Gill, Muscle and Liver of a Freshwater Mudfish *(Parachanna Obscura*) from Ogba River, Benin City, Nigeria. African Journal of Biotechnology, 6: 2620-2627.

Olaifa, F. G.; Olaifa, A. K.; Onwude, T. E., (2004). Lethal and Sub lethal Effects Of Copper to the African Cat Fish *(Clarias Gariepnus). African Journal of Biomedical Research*, 7, 65-70

Olaifa F.E, Olaifa A.K, Adelaja. A.A, and Owolabi A.G. (2004). Heavy Metal Contamination of Clarias Garpinus from a Lake and Fish Farm in Ibadan, Nigeria. *African Journal of Biomedical Research* 7: 145-148.

Otitoloju A.A and Don-Pedro K.N. (2004). Integrated laboratory and Field assessments of Heavy metals Accumulation in edible Periwinkle,*Tympanotonus fuscatus* Var.Radula(L),Ecotoxicology and Environmental Safety 57:354-362.

Osmond, D.L, Line, D.E, Gale, J.A, Gannon, R.W., (1995). Water, Soil and Hydro-Environmental Decision Support System.

Oyowe .E.O. (1998).industrial Sources and Distribution of Heavy metals in Lagos Lagoon and their Biological Effects on Estuarine Animals.Ph.D.Thesis, University of Lagos, Lagos.

Pelgrom, S., Lamers L., Lock, R., Balm P. and Bonga S.W., (2002). Integrated Exposure Aquaticic Toxicology,32: 303-320.

Perin G, Craboledda L, Lucchese M, Cirillo R, Dotta L, Zanetta ML, Oro, A,A (1985).

Heavy Metal Speciation in the Sediments of Northern Adriatic Sea. A New Approach for Environmental Toxicity Determination.

Pohl,C; Kattner,G.; Schulz.Baides, M. (1993). Cadmium, Copper, Zinc On Transects Through Aretic and Easter Atlantic Surface and Deep Waters. *Journal of Marine*. 4; 17-29.

Poulton, B. C., Monda, D.O. and Brumbaugh, W.G. (1995). Relations between Benthic Community Structure and Metals Concentrations in Aquatic Macroinvertebrates. Clark Fork River, Montana. *Journal of fresh water Ecology*.10: 277-293

Ramirez, M., Serena, M., Franche, R. and Correa, J.(2005).Metal Speciation and Environmental Impact On Sandy Beaches Due To El Salvador Copper Mine, Marine Pollution Bulletin, 50:62-67

Rauret, G. (1998). Extraction Procedures for the Determination of Heavy Metals in Contaminated Soils and Sediments, Talanta, 19:67-79.

Republic of Kenya,Ministry of Planning and National Development (1999). District Development Plan.Uasin Gishu District.Government Printers, Nairobi, Kenya.

Rout, G.R., and P. Das. 2003. Effect of Metal Toxicity on Plant Growth and Metabolism: Zinc. Agronomie 23:3-11.

Saeed, S.M and Sakr. S. F. (2008). Impact of Cage- Fish Culture In The River Nile On Physico- Chemical Characteristics Of Water, Metals Accumulation, Histologigal And Some Biochemical Parameters In Fish. *Abbassa International Journal of Aquatic, (1A):179-202.*

Sarika, P.R. and Chandramohankumar, (2008). Geochemistry of Heavy Metals in the Surficial Sediments of Mangroves of the Southwest Coast of India. Chemical.

Ecology 24: 437-447.

Senavathne. P and K.A.S. Pathiratne (2007). Accumulation Of Heavy Metals In Food Fish,Mystus Gulio Inhabiting Bolgoda Lake, Srilanka.

Shitshama,J.M and Tole. M.P (2003) Heavy metal contaminants in Fish,Water and Sediments in Lake Victoria, Kenya.

Soares, HMVM., Boaventura, RAR., Machado, AASC. & Esteves de Silva, JCG. (1999). Sediments as Monitors of Heavy Metal Contamination in the Ave River Basin (Portugal): Multivariate Analysis of Data. Environmental Pollution 105: 311–323.

Singh, K.V, Singh, P.K, and Mohan, D. (2005). Status of Heavy Metals in Water Journal Of Soil Science Environmental Management and Bed Sediments of river Gomti-a tributary of the Ganga River, India. Environmental Monitoring Assessment 105: 43-67

Stecko, J. R. P. and Bendell-Young, L. I. (2000) Contrasting the geochemistry of Suspended particulate matter and deposited sediments within an estuary, Applied Geochem., 15: 753-775.

Suziki, Y. Nogi,A and Fukasawa.(1988). Gall L Protein,and auxillary Transcription activator for Genes Encoding Galactose-Metabolizing Enzymes in *Saccharomyse cereuisiae*,Molecular and Cellular Biology 8:4991-4999.

Zakir, H. M. (2008). Geochemical Partitioning Of Trace Metals: An Evaluation of Different Fractionation Methods and Assessment Of Anthropogenic Pollution In River Sediments. Ph D thesis, Keio Univ.Yokohama 223-8522, Japan

Tessier, A., Campbell, P. G. C. and Bisson, M. (1979). Sequential Extraction Procedure For The Speciation Of Particulate Trace Metals, Analitical Chemistry, 51: 844-851.

Tsai, L.J., Yu, K.C., Chen, S.F. and Kung, P.Y (2003). Effect Of Temperature On Removal of Heavy Metals from Contaminated River Sediments Via Bioleaching Water Research, 37: 2449–2457

Turner A, (2000). Trace Metal Contamination In Sediments From U.K. Estuaries: An empirical evaluation of the role of hydrous iron and manganese oxides. Estuarine, Coastal and Shelf Science, 50: 355–371.

Ubaidullah, M., Javed, M. and Abdullah, A. (2004). Metals Toxicity of Sediments in the River Ravi and Related Effluents Discharging Tributaries. Industrial Journal of Biological Science, 1: 43–49

Ubaidullah, M., Javed, M. and Abdullah, S. (2004). Metals Toxicity of Sediments in the River Ravi And Related Effluents Discharging Tributaries. *Industrial Journal Biological Science*, 1: 43–49

USEPA, (United States Environmental Protection Agency) (1999) National Recommended Water Quality Criteria- Correction EPA *822/Z-99.001*, Washington DC.

Van Der Sloot, H.A., Heasman, L. And Querasviller, P.H. (eds.) (1997). Harmonization Of Leaching/ Extraction Test 5:75-99

Waqar, A., (2006). Levels of Selected Heavy Metals in Tuna Fish. *Arabic Journal of Science Engineering*, 31 (1A), 89–92.

Weisz M., Wenzel W.W. and Stingeder G.J. (2004). Determination Of Trace Elements Bound To Soils And Sediment Fractions, (IUPAC Technical Report). Pure Applied Chemistry, **76**(2), 415

Welch.EB. (1992). Ecological Effects of Waste Water. Applied Limnology Of Pollutant Effects 2nd Edition. New York

World Health Organization (WHO). (1984). Guidelines for drinking water Quality Volume 1. Recommendations, Geneva.

World Health Organization (WHO). (1988). Chromium, International Programme on chemical safety. Environmental Aspects, Environmental Health criteria, Geneva.pp196

Zar H. (1984). Biostatistical Analysis. Prentice Hall International Inc. New Jersey Englewood Cliffs.pp150-153,261-263

# APPENDIX 1

## One way ANOVA for Heavy Metals

| Element | P | F |
|---|---|---|
| Copper sediment | 0.002 | 35.79 |
| Water | 0.07 | 3.36 |
| Plant | 0.001 | 102.2 |
| Lead sediment | 0.0009 | 12.3 |
| Water | 0.0004 | 85.4 |
| Plant | 0.0006 | 8.16 |
| Zinc sediment | 0.059 | 3.73 |
| Water | 0.05 | 18.05 |
| Plant | 0.65 | 0.21 |

# APPENDIX 2

*Polygonum pulchrum* growing naturally by the river bank (Source:Author,2012)