SPATIAL AND TEMPORAL VARIATIONS IN PHYSICO-CHEMICAL PARAMETERS, NUTRIENTS AND HEAVY METALS ALONG A GRADIENT OF ANTHROPOGENIC ACTIVITIES WITHIN KAPSABET RIVER, KENYA

BY

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DECLARATION

Declaration by the student

This thesis is my original work and has not been presented for a degree in any other University. No part of this thesis may be reproduced without the prior permission of the author and/or University of Eldoret.

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This thesis is dedicated to my parents, Joseph Kiplimo Lelei and Dorcas Jeruto Lelei, who sacrificially educated me and contributed greatly to my success.

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ABSTRACT

Increased human activities have led to water pollution, especially metals and nutrients. Therefore, prudent management of aquatic environments require information on their quality status that can be estimated by monitoring water to determine extent of pollution. This study examined the spatial and temporal variations of heavy metals and nutrients in water, soil and sediments which were sampled along four sites (S1, S2, S3 and S4) as Kapsabet River flows from upstream to down stream for both dry and wet season. The parameters analyzed were: temperature, pH, chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS) and total suspended solids (TSS) while phosphates and nitrates were the nutrients analyzed. Heavy metals analyzed included Pb, Cu, Fe and Zn using atomic absorption spectroscopy (AAS). TSS and TDS were determined by gravimetric method, COD titrimetrically, BOD by incubation, phosphates and nitrates by colorimetric method. Data was analyzed statistically using SPSS computer package. All parameters analyzed increased downstream, except Cu, with maximum mean values recorded in wet season. Their spatial and temporal values were: in water, pH (7.2 -10.3), TSS (110 -1301 mg/L), TDS (868 - 2990 mg/L), COD (6.0 – 67 mg/L), BOD (3.0 - 33.7 mg/L) PO_4^{3-} (0.2 - 2.1 mg/L) and NO_3^- (0.6 - 4.5 mg/L), in soil and sediments, PO_4^{3-} mean values were: 0.5-1.8 mg/L and 0.7 – 2 mg/L, respectively, while NO_3^- in soil and sediments were: 5-5.2 mg/L and 8-8.0 mg/L, respectively. For heavy metal, Fe had high concentration with mean values in water, soil and sediment being, 0.19 – 12.02 μg/g, 1.15 – 38.78 μg/g and 0.12 – 69.89 μg/g, respectively, while Cu had the least concentration with mean values being, 0.017 - 0.174 μg/g, 0.008- 0.424 μg/g and 0.08 - 3.056 μg/g in water, soil and sediments, respectively. There was significant ($p < 0.05$) spatial and temporal distribution of metals along the river profile. In both water and sediments, S3 and S4 contained significantly ($p < 0.05$) the highest concentrations of Pb, Fe and Zn associated with anthropogenic pollution. Based on the results obtained Kapsabet river water is not safe for drinking and other domestic uses and therefore, it is recommended that a for nutrient reduction strategy be undertaken, for example, construction of buffer zone.

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LIST OF ABBREVIATIONS

AAS- Atomic absorption spectroscopy

AFS- Atomic fluorescence spectroscopy

BOD- Biological oxygen demand

COD- Chemical oxygen demand

EMC- Eldoret municipal council

KARI- Kenya agricultural research institute

KWS- Kenya wildlife service

NEMA- National environmental management authority

NPSD- National policy for sustainable development

NSCT- National council of science and technology

TDS- Total dissolved solids

TSS- Total suspended solids

WHO- World health organization

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the study

As the country focuses towards achieving middle-income status by 2030, it is imperative that the government raises public awareness on management of chemical substances. Chemicals are used in life-saving medicines, purification of drinking water and also in farming as fertilizers. In rural areas, where three-quarters of the world's poor live, most chemical exposure is linked to polluted water sources as well as use of fertilizers in agriculture (Geoffrey, 2011). Information on water quality and pollution sources is important for the implementation of sustainable water-use management strategies (Crosa *et al*., 2006; Sarkar *et al*., 2007; Zhou *et al*., 2007). In addition, due to seasonality and regionality of river water, assessing spatial and temporal variations of river water quality at a watershed level has become an important aspect for the physical and chemical characterization of aquatic environments (Ouyang *et al*., 2006; Sundaray *et al*., 2006).

Rivers play a significant role within a landscape as they are at the receiving end of all the human activities within their catchments. Therefore, the character of streams and rivers reflect an integration of physical, chemical and biological processes occurring in the catchments. Landscape properties that contribute most directly to the aquatic systems include riparian land use, cover patterns, quaternary and bedrock geology, and hydrography (Townsend *et al*., 2003). Landscape form and composition play a major role in regulating stream chemistry. Landscape-level processes define the overall supply of elements to a stream and provide the framework within which other processes operate on smaller spatial scales and shorter temporal scales to regulate supply and availability

(Abira *et al*., 2008). The availability and cycling of nutrients within a riverine environment is very important in the functioning of the ecosystems. Analysis of the changes in river water quality often reveals the impact of different activities taking place within a river basin.

Human activities are responsible for fundamental changes to riparian of stream catchments around the world. For instance, conversion of natural forest to agriculture may influence stream water chemistry (Smith *et al.,* 2005). Deforestation can increase light levels, and thus enhance algal productivity but decrease inputs of woody debris, leaves and other coarse particulate organic matter (Kannel *et al.,* 2008). Changes in land use that affect riparian vegetation can, therefore, be expected to have important consequences for the physico-chemistry of stream water. Yet in the last decades, industrialization, urbanization and exponential population growth have become critical to these water bodies. As such, water quality problems are not new in most ecosystems of the world but have been recently aggravated by these adverse anthropogenic impacts (Caccia and Boyer, 2005; Zhang *et a*l., 2009). The scarcity of clean water and pollution of fresh water has therefore led to a situation in which one fifth of the urban dwellers in developing countries and three quarters of their rural dwelling population do not have access to reasonably safe water supplies (Lioyd and Helmer, 1992).

The human activities including indiscriminate use of inorganic fertilizers during agriculture, disposal of waste products such as detergents and discharge of pollutants from the mining zones, transport of nutrients and pesticides have resulted in changes in water quality of rivers resulting in increased levels of pollutants into recipient water

bodies with consequential drastic changes in the watershed health. Since the internal ecosystems of the water bodies in rivers are intimately tied to the physical, chemical and biological processes within the entire watershed, health status of rivers often depict the cumulative effects of the water quality changes originating from the catchment areas (Gantidis *et al.,* 2007).

The point and non-point source pollution arising from sources that are normally associated with agricultural and silvicultural activities within the catchments are transported from land by atmospheric, surface water and ground water pathways. Moreover, the concern of elevated levels of toxic metals have continued in water, soils and sediments (Luoma and Rainbow, 2008; Khan *et al*., 2008; Hang *et al*., 2009; Zheng *et al*., 2010). It is these changes in quality of water parameters and the elevated levels of toxic metals in the aquatic systems that continue to pose problems of increasing environmental concern. As a result of these perturbations, there is an increased interest in holistic evaluation of the quality status of water in both lentic and lotic systems (Chindah, 2012).

For many years, Africa was considered safe from heavy metal pollution and related contaminant (Biney *et al*., 1994). However, rapid population growth and high urbanization rates have resulted in a recent expansion of cities in the absence of proper planning and without adequate waste disposal facilities (JICA, 2002). Therefore, increased reports of adverse changes in water quality and increasing concentrations of toxic metals are reported and may not be further ignored by the environmental managers. There are limited resources for environmental management in Kenya, as most

developmental programs are focused on increasing food security, economic growth and industrialization (Snoussi and Awosika, 1998). Consequently, industrial expansion and increased extraction of natural resources have resulted in widespread water pollution affecting previously pristine aquatic ecosystems (Ramesh *et al*., 2007). To get a true reflection of what happens within the catchments of a river basin either through point or non-point sources of pollution, studies of spatial and temporal changes in water quality and concentration of the heavy metals are vital.

There are numerous studies that have been conducted in Kenya. Based on these studies, ominous signs of water quality changes and increased metal pollution have been documented due to agriculture, urbanization, human settlement, motor vehicle wastes and industrial activities (Wandiga, 1981; Wandiga *et al*., 1983; Wandiga and Onyari, 1987; Onyari and Wandiga, 1989; Onyari *et al*., 1991; Mwamburi and Oloo, 1997; Mwamburi, 2003; Raburu, 2003; Raburu *et al*., 2009). Yet, most of these studies have been conducted in large basins and rivers in Kenya, ignoring the potential of water quality and heavy metals problems in the upstream water bodies, which have continued to be exposed to myriads of anthropogenic activities.

As a case in point, numerous reports for instance Lacher *et al*., (1997) indicated that chemical fertilizers are used extensively in agriculture, in order to improve yield and productivity of agricultural products in most of the upland streams. Kapsabet in the Rift Valley Province of Kenya is an agricultural urban area and information available in grey literature indicates that there is extensive use of chemical fertilizers in the catchments and livestock production. Yet there is lack of studies on how these activities continue to affect

the quality of water in the recipient Kapsabet River. For this, the current study was therefore undertaken to document the water quality along an upstream Kapsabet River through an analysis of the physico-chemical parameters, nutrients and heavy metal content and distribution in riverine water, soils and sediments.

1.2 Statement of the Problem

Pollution of water bodies and riverine ecosystems is a worldwide problem (Bryan, 1992; Onyari *et al*., 1991; Ober *et al*., 2007). In recent times, the increased problems of water quality changes and increased occurrence of metal contaminants especially the heavy and toxic metals in excess of natural loads has become a problem of increasing concerns in aquatic habitats and is a common feature in many parts of the world. The pollutant levels found in these habitats can be influenced either by natural or anthropogenic sources. Irrespective of the source of the pollutants if the levels are higher than recommended background levels, the abiotic and biotic component of the environment will be affected in one way or the other. To mitigate these problems in the aquatic environment, up to date information on the levels of pollution is important. Yet for many upstream water bodies in Kenya such studies are out rightly lacking or sporadic and not scientifically documented. The paucity of data on water quality of these rapidly changing environments due to evidence of increased anthropogenic signatures will continue to subtend planning of pollution control strategies. Due to increasing modern agricultural activity and high population along the water catchments area within the past few years, the quality of water of Kapsabet River may be impacted. Thus, absence of research on water quality of the river will continue to expose the residents to pollution due to consumption of water with poor quality and toxic metals.

1.3 Justification of the Study

Limnological information obtained from this study can be used to suggest measures that can be taken to correct any problem that may be associated with land use patterns and changes within the catchments. Moreover, the study is geared towards setting up database from which more precise quality criteria may be formulated. The comparison of the physico-chemical and heavy metal levels of the Kapsabet River water with the national/international water quality standards would indicate the degree to which the upstream river is affected by the environment pollution, which should signal the need for remedial measures. Monitoring programmes could then follow in future to detect changes and compliance with standards.

Also analysis and findings of this study are envisaged to be useful in helping resolve the perennial problems inherent in polluted upstream river where the population will benefit the riparian and the local populations interacting with it most. Data generated by the study will lend legitimacy to an advanced discussion on environmental issues with stakeholders, hence providing a reliable and excellent basis for building and improving lasting relationship among stakeholders.

1.4 Objectives

1.4.1 General Objective

The main objective of the study was to obtain information on the limnology of Kapsabet River in order to get baseline data on the spatial and temporal variation in the physico-chemical parameters, nutrients and heavy metal distribution in water, soil and sediment.

1.4.2 Specific Objectives

The specific objectives were:

1. To determine the spatial and temporal changes in the physico-chemical parameters (pH, BOD, COD, TSS and TDS) in water, soils and sediments.

2. To determine the spatial and temporal changes in the levels of nutrients (nitrates and phosphates) in water, soils and sediments.

3. To determine the spatial and temporal changes in the levels of heavy metals (Pb, Cu, Zn and Fe) in water, soils and sediments.

1.5 Hypotheses

1. There are no significant spatial and temporal changes in the physico-chemical parameters (pH, BOD, COD, TSS and TDS levels) in water, soils and sediments.

2. There are no significant spatial and temporal changes in the levels of nutrients (nitrates and phosphates) in water, soils and sediments.

3. There is no significant spatial and temporal changes in the levels of heavy metals (Pb, Cu, Zn and, Fe) in water, soils and sediments.

1.6 Study area

1.6.1 Background and location

The study was conducted in Kapsabet River which passes within Kapsabet town (Figure 1.1). It is situated within the latitudes; $0^0 13^{'}$ N, longitude; $35^0 08$'E and lies between 1975-2700 m above sea level with average slope of 4 per 1000. There is ongoing construction of water treatment plant for Kapsabet municipality along this river. Water from this river serves the residents of the rapidly growing Kapsabet town.

S1

Tributary

ELDORET - *KAPSABET ROUTE*

CHEPTERIT
CENTRE

S2

SUDAN

ETHIOPIA

UGANDA

TURKANA

MARSABIT

MANDERA

WAJIR

SAMBURU

ISIOLO

SOMALIA

WEST POKOT

BARINGO

LAIKIPIA

MERU

NAKURU

NYERI

THARAKA

EMBU

GARISSA

NAROK

MACHAKOS

KITUI

TANA RIVER

KAJIADO

MAKUENI

LAMU

TANZANIA

TAITA-TAVETA

KILIFI

INDIAN OCEAN

KWALE

MOMBASA

BRIDGE

S3

KAPSABET RIVER

KAPSABET TOWN

N

KAMOBO AREA

KEY

S4

S1 A point upstream before water enters the town

S2 A point where water enters the town

S3 A point where water leaves the town

S4 A point downstream after leaving the town

Figure 1.1: Sketch Map of Study Area (Source: Author, 2012)

The region receives an average of 1350 mm/year of rain and is an important cereal and tea- farming region of Kenya (NPSD, 2010). Potential major sources of pollution for the Kapsabet River basin are the agricultural chemicals and urban effluents of Kapsabet town.

1.6.2 Human activities

The main socio-economic activities in the study area include industrial activities such as Chebut tea factory, agrochemicals and agriculture, the latter being practiced on both sides of the riverine wetlands of Kapsabet River. At Kapsabet, food crops such as maize, sweet potatoes and cassava, sorghum, millet and vegetables are grown on small-scale farms, usually extending up to the Kapsabet River banks. Livestock farming is practiced and the Kapsabet River provides water for both domestic and livestock use. Small scale fishing in the river water is also practiced. Chebut tea factory is situated at Kapsabet, which is within the Kapsabet River catchment, and draws large volumes of water from the river for industrial use and discharges it back to the river as effluent at a distance of 2 km downstream of the water intake point.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Dynamics of physico-chemical environments in aquatic systems

The major driving forces controlling the physical and chemical composition of the water in the aquatic environments are the age-old processes of rainfall, erosion, dissolution, evaporation and sedimentation as well as biological components of watershed. This has necessitated varied numbers of limnologists to monitor physical and chemical parameters in aquatic ecosystems (Goldman and Horn, 1983; Wetzel, 1983; Burgis and Morris, 1987). The major physical factors that usually affect the aquatic environments significantly includes; temperature, hydrogen ion concentrations (pH), Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) (Burgis and Morris, 1987). Among these factors, variations in temperature and pH usually have the most profound (and sometimes lethal) effects on the aquatic environment. This is because they have a direct influence on the physical, chemical and biological functions of organisms (Lickens, 1975; Alvarez, 2000).

Water temperature changes; even as low as 0.8 °C have been found to be harmful and even lethal to some aquatic environments in a very short period of time. High water temperatures also contribute to decreased amounts of dissolved oxygen sometimes to a level below the point necessary to sustain many animals. Exceedingly high temperature in water is associated with perennial surface water problems such as water taste, odour, colour and corrosion (WHO, 1984); so that temperature fluctuations in a water body such as Kapsabet River should be taken seriously because in the long run, this can lead to

significant changes in the flora and fauna of the river as already pointed out by a Kenya Government Report in River Nzoia (Republic of Kenya, 1981).

Water in the aquatic environment also contains hydrogen ions that ultimately influence the pH values of the system. The pH of a water body is a measure of the concentration of hydrogen ions in it (Smoot *et al*., 1995). It is the measure of the acid balance of a solution and is defined as the negative of the logarithm to the base10 of the ion concentration. That is;

$$pH = -Log_{10}[H^+] = Log_{10}(1/[H^+])\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..\ldots\ldots\ldots\text{Equation 2.1}$$

Water dissociates to only a slight degree yielding hydrogen ions equal to 10^{-7} mol/L, hence pure water has a pH of 7. This water is also neutral since 10^{-7} mol /l of hydroxyl ion produced according to the equation:

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..\text{Equation 2.2}$$
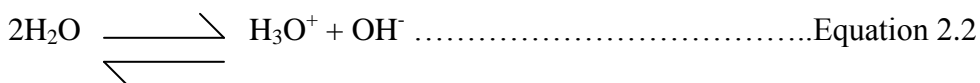
Lower pH values indicate high acidity and higher pH values indicate alkalinity. Rivers, which receive water that has flown over or through rocks and soil rich in carbonate ions; have high pH (Kalff, 2002). Water with high concentration of calcium carbonate and calcium bicarbonate is called 'hard' water. Extremely 'hard' water has pH often exceeding 9.

Many chemical reactions are controlled by pH and biological activity is usually restricted to a fairly narrow range of 5−8 (Tebbult, 1998). High or low pH values in rivers have been reported to affect aquatic life and alter toxicity of other pollutants in one form or the other. The concentration of H^+ ions in water normally ranges from 0 (very acidic) to 14

(very alkaline). However, the pH of most natural water lies between 5.0 to 8.5 units (Hem, 1985). The pH of natural water system is as a result of the acid-base equilibrium achieved by various salts and gases dissolved in it (Smoot *et al*., 1995). An influx of either acid or alkaline wastes can cause the pH of natural water to become lower or higher than the neutral pH (7.0) point. The discharge of highly alkaline or highly acidic waste water into a water body therefore causes alterations in the pH of the water body (Boyd, 1992).

Dissolved oxygen (DO) is critical aspect of water quality indicating the health of an aquatic system because aquatic organisms need oxygen to survive. Aquatic organisms are able to extract DO from the water medium. Distribution of oxygen in water of a lake is the product of interacting factors between the prevailing temperature and the presence of aquatic flora that utilize carbon dioxide and release oxygen during photosynthesis (Wetzel, 1983). The amount of DO in the water is a factor in determining the species and abundance of organisms that can live in a water body (Kamau, 2002). DO levels are influenced by temperature and salinity, which are also influenced by climatic and geological dynamics, respectively. The solubility of oxygen, or its ability to dissolve in water, decreases with increasing temperature and salinity (Kalff and Knoechel, 2002). Aquatic organisms in the swamps are able to extract dissolved oxygen from the water medium. The optimum level of DO is 9 mg/l (Hopko, 2011).

Water undergoing intense anthropogenic disturbances usually exhibit marked changes in the DO values. Biological oxygen demand (BOD) is any oxidizable materials present in

natural water way or in industrial waste water that will be oxidized both by biochemical (bacteria) or a chemical process. These biochemical reactions create what is measured in the laboratory as BOD (Tchobanogluos *et al*., 2003). It measures the oxygen demand of biodegradable pollutants (organic matters). The greater the decomposed matter present, the greater the oxygen demand and the greater the BOD value (Ademoroti, 1996). Samples for BOD analysis may undergo significant degradation during handling and storage that may reduce the change in oxygen demand. Therefore samples for BOD should be kept below $4^{\circ}C$ and begin incubation not more than 24 hours after the sample is collected. Work done by German consultant for Eldoret municipal council in 1986 and 1987 gave BOD of 20, 70, 10 and 5 mg/L on four different sites for River Sosiani downstream (distance not specified) (EMC VOL. 1, 1989).

Chemical oxygen demand (COD) exemplifies the oxidizable chemicals such as reducing chemicals which when introduced into natural water will initiate chemical reactions creating what is measured as the COD (Tchobanoglous *et al*., 2003). It measures the oxygen demand of biodegradable pollutants plus the oxygen demand of non-biodegradable oxidizable pollutants. During the determination of COD, organic matter is converted to CO_2 and water, amino nitrogen converted to ammonia nitrogen and organic nitrogen in higher oxidation states converted to nitrates regardless of the biological degradability of the substance (Greenberg *et al*., 1992).

However, recent comprehensive limnological surveys in many upstream rivers are scanty, only present in form of sporadic Kenya wildlife service (KWS) survey reports that are

rarely availed to most stakeholders. Paucity of such recent data limits extended knowledge about the limnological status of these rivers that ultimately affects management.

2.2 Variations in nutrients in the environment

Nutrient is another important chemical factor in the most aquatic ecosystems (Goldman and Horn, 1983; Burgis and Morris, 1987; Alvarez, 2000). The most important nutrients in rivers being those, which are often short in supply and which limit growth of plants. Both nitrates and phosphates are essential to life processes (Reynolds, 1984) but while there are many sources of nitrate, phosphate is often short in supply and therefore limiting to plants growth (Goldman and Horn, 1983; Wetzel, 1986; Burgis and Morris, 1987).

In natural waters, nitrogen (IV) is commonly found in combined form as nitrates. Usually through the biological process of denitrification in anaerobic conditions nitrates may be reduced to nitrites. Drinking waters containing high nitrates can cause infant methamoglobinaemia (blue baby syndrome). It is a condition where the ability of blood to absorb oxygen is impaired. Study to determine the impact of agricultural activities on the nutrients levels on a section of Migori River, which rises and discharges into Lake Victoria in Migori district, Nyanza province, was carried out, the results obtained showed that the nutrients levels were above the WHO, 1996 recommended limits (Mbovu *et al.*, 2004). This was occasioned by the fact that residents depended almost entirely on the raw, untreated water for their day-to-day needs. Upstream of the river is an active

agricultural region mainly under tobacco, sugarcane and subsistence crops. Kalff (2002) suggested that although nitrogen was usually abundant in temperate aquatic regions, it could be a limiting nutrient in a number of tropical aquatic ecosystems. Bioassays and limnological studies performed in a number of rivers usually indicate that nitrate, phosphate or both limit primary production (Davis *et al.*, 2003), the availability of these two nutrients within the river ecosystem depends not only on allochthonous sources of nutrients but also from autochthonous biological processes within the river itself.

Nitrogen must be converted to ammonia, nitrates or some organic forms before most organisms can use it. Nitrate is the most highly oxidized form of nitrogen and is usually the most abundant and important form of combined inorganic nitrogen in rivers (Goldman and Horn, 1983). Since, nitrates are transported in highly soluble forms by either clear or muddy water hence high concentration tends to occur in water than other forms of nitrogen (Yang *et al.*, 2010; Cuihong *et al.,* 2011).

Wetzel (1986) reported that the principal forms of nitrogen for phytoplankton growth are nitrate, nitrite, ammonia and urea. Low nitrate concentration reported in a variety of African water bodies by Vareschi (1982) suggested a potential nitrate limitation of production. Heterotrophic bacteria generate NH_3-N as a primary end product of decomposition of organic matter (Goldman and Horn, 1983). Its distribution in aquatic ecosystems is highly variable and depends upon the level of productivity of rivers and the extent of pollution from organic matter (Wetzel, 1983). Concentration of NH_3-N in well-

oxygenated waters is usually low as algae rapidly assimilate it and this represents the most significant source of nitrogen for plankton in many rivers (Girija

et al., 2007).

Phosphorus enters rivers via rainfall, from upstream and other influents from surrounding land (Cech, 2010). The author further notes that phosphorus is generally transported as phosphates adsorbed in the soil particles especially from agricultural areas. The phosphorus released in water enables more algae to grow and when they die, they use up more of oxygen from the water just above the surface of the mud during decomposition (Kalff, 2002). According to Tufford *et al.*, (2003) three types of phosphates are normally measured in aquatic ecosystems: dissolved phosphates, total phosphorus and particulate phosphorus. Despite the varied nature of many phosphorus compounds, aquatic plants can only absorb phosphorus as dissolved inorganic phosphates. Only dissolved phosphate can be used directly for algal growth and in this form, it is called reactive soluble phosphorus.

In comparison to the rich natural supply of other major nutritional and structural components of the biota, phosphorus though needed in small amounts is least abundant, due to its geochemical shortage in drainage basins. Thus the availability of phosphorus is the limiting factor that controls the rate of plants growth and therefore productivity of the whole plant community (Odum, 1983). Hutchinson (1975) and Wetzel (1983) concluded that phosphorus is more likely to limit primary production in rivers than any other nutrient because of its major role in biological metabolism. Phosphorus limitation of

primary productivity has been shown for a majority of oligotrophic and mesotrophic rivers (Peterjohn and Correll, 1984).

Phosphorus occurs naturally as the mineral apatite in igneous rocks and as phosphate rock, a chemical sedimentary rock. Phosphates are also used widely in cleansing agents and in water and waste water treatment. Despite the varied nature of many phosphorus compounds, plants can only absorb phosphorus as dissolved inorganic phosphates (PO_4^{3-}) (Nicolau *et al.,* 2006).

2.3 Dynamic of metals in the environment

There are 35 metals that are of concern because of occupational or residential exposure; 23 of these are the heavy elements or heavy metals. "Heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water and constitute less than 1% of the rocks in the earth's crust (Glanze *et al.,* 1996). Such elements include Zn, Pb, and Cu, Cr, Cd, Fe, B, As, Ce and Hg among others (Manahan, 1992). They are released into the environment naturally by weathering and by volcanic eruptions or artificially by anthropogenic activities such as agriculture, industrial activities and transport. Usually heavy metals accumulate in soils, water, plants and crops, eventually finding their way into humans through the diet. Once in human, they tend to cause variety of health complications. Source, pathways and effects of heavy metals are reviewed in this section alongside studies relating to heavy metals in the global environments.

2.3.1 Sources and distribution of metals in the environment

Heavy and toxic metals are widely distributed in the global environments. Certain areas of the global environment have higher concentration reminiscent of the human activities in those areas. In vast majority of countries especially in Africa where certain environments are almost pristine have levels of heavy metals that may be considered to be below threshold. Some of the natural sources of heavy metals in soil, water and sediments are chemical and physical weathering of igneous and metamorphic rocks and soils. Other contributions include the decomposition of plant and animal detritus, precipitation or atmospheric deposition of airborne particles from volcanic activity, wind erosion, forest fire smoke, plant exudates, and oceanic spray. Anthropogenic sources include surface runoff from mining operations, which usually has a low pH and contains high levels of metals such as Fe, Mn, Zn, Cu, Ni and Co. The combustion of fossil fuels pollutes the atmosphere with metal particulates that eventually settle to the land surface. Urban storm water runoff often contains metals from roadways and atmospheric fallout. Currently, anthropogenic inputs of metals exceed natural inputs. Point sources including domestic wastewater effluent containing metals from metabolic wastes, corrosion of water pipes, and consumer products, industrial effluents and waste sludges may substantially contribute to metal loading (Pacyna, 2005). Once in the environment, metals are partitioned among the various aquatic environmental compartments (water, suspended solids, soils and biota).

The metals in the environment may occur in dissolved, particulate and complexed form. The main processes governing distribution and partition are dilution, dispersion,

sedimentation, and adsorption/desorption (Luoma and Rainbow, 2008). Nonetheless, other chemical processes could also occur. Thus speciation under the various soluble forms is regulated by the instability constants of the various complexes and by the physico-chemical properties of the water such as pH, dissolved ions and temperature (Apostolis *et al*., 2007). In the course of distribution, permanent or temporary storage of metals takes place in the environmental media. Microbial activity and redox processes may change the properties of soils and affect the composition of interstitial water and eventually, to the final consumer of the particles containing heavy metals (McBride, 2007). Biological processes reworking the soils will also bring soils to the surface, where a significant fraction of the metal will be released for use by the flora and fauna that eventually have a bearing on the heavy metal content to the human environment.

Spatial and temporal variations of heavy metals in African countries have been studied extensively in water and soils; with sporadic study protocol convferging in humans. However, of the above different media matrices, soils have been more analyzed because they can present a clearer indication of metal inputs and accumulation in the environments. This section will therefore present studies of heavy metal concentration in water, wet sediments and soils. It presents information in the global environments, African context and in Kenya (Wetzel, 2001).

2.3.2 Distribution of metals in water media

Water covers 75% of the earth surface and supports a large biotic assemblage. Many of the industrial process in the world proceed in presence of huge quantity of water for

running the processes. Therefore as long as humans continue to exert industrial pressure on these water resources, aquatic environmental concerns will continue to be an issue. To date, a number of studies have established the distribution of metals in water within the global environments (Chindah, 2012).

In the United States of America, for instance, a wide distribution in the concentration of metals in water samples around the country was established. The average values of the studied metals; Fe, Pb, Zn and Cu in the water samples analyzed were higher than the respective reference values obtained in pristine environments. Further, temporal variations in the distribution of metals established that during summer, elevated levels of all metals were recorded (Ikem *et al*., 2003). Elsewhere, a non-uniform spatial distribution of ten metals (As, Cd, Co, Cu, Fe, Hg, Rb, Sb, Se, and Zn) was reported in polluted and unpolluted waters of the British Isle. In this environment, elevated concentrations of Hg were found close to Mytelene Harbour in the island of Lesvos (Apostolis *et al*., 2007).

River waters have been used in many countries as a source of drinking water and studies of heavy and toxic metals in the countries are also numerous. The seasonal distribution of dissolved and particulate metals in the water column of the Damietta branch of the River Nile depicted a heterogeneous spatial and temporal distribution pattern of metals (Fahmy, 1981; El-Rayis and Saad, 1985). In Ghana, drinking water from the Obuasi gold mining area was found to contain As concentrations above normal values in relation to such water from other parts of the country. It was further established that during rainy seasons

the levels of metals in drinking water were lower than values reported during dry seasons (Amasa, 1975). Later, but in the same country, gold mining activities were generally found to elevate metal concentrations in water (Bamford *et al*., 1990). Investigation of the distributions of metals in drinking water from two South African rivers; Hartbeespoort dam, and Voëlvlei dam showed that for all the metals studied, higher levels of concentration occurred in Hartbeespoort dam than in Voëlvlei. Moreover, the seasonality in concentration of the metals was also distinct during the rainy seasons when compared to dry seasons (Greichus *et al*., 1978). In Uganda, the concentration of Cu in the surface waters of Lake George was higher than that in Lake Edward. Similarly, a significant shift in metal concentrations during seasonal cycles was highlighted for the two rivers (Bugenyi, 1979).

Studies and publications exist for metals in water among a variety of water bodies in Kenya. Considering that many people in Kenya use lakes, rivers and dams as a source of drinking water, information on metals in a variety of water bodies can provide indirect linkages with the levels of metals in humans. Early studies concerning metals in water focused on water from lake Nakuru, Kenya, one of a number of volcanic Soda lakes in the Great Rift Valley. In an attempt to produce baseline information for monitoring pollution, results of the concentrations of metals; As, Sb, Cu, Zn, Cd and Hg in the lake have been documented (Koeman *et al*. 1972). It was established that metal concentration within the lake varied widely even though the water body was small and prone to complete wind mixing. Temporal variations in metal concentrations were also found to be significant within the water in the aquatic environments. Though the lake was gazetted

later on, and therefore use of the water for drinking by humans eliminated, earlier evidence suggested that people used the water for drinking purpose in the 1970s against the existing laws prohibiting such water use (Vareschi, 1982). Later studies in the vicinity of the area looked at the metal concentrations in drinking water from River Njoro where differences in distribution of Cu, Pb, Cd and As along a gradient of human activities were reported. Heavy rains were also found to increase the levels of metals especially in the stations situated in the lower reaches of the river (Ndaruga *et al*., 2004).

Unlike for lacusterine and oceanic water sources, many people staying around riverine environments depend on the water for their domestic uses. Therefore studies of the concentrations of metals in water in such environment are important determinants of metal levels in the humans. Earlier studies on drinking water from Lake Victoria showed no significant differences in spatial distribution of metals (Alala, 1981; Onyari and Wandiga, 1989). However, more recent studies of water from the same area revealed increased diversity in distribution of Pb, Zn and Hg levels within the lake (Ochieng, 2007). Moreover, the seasonal differences are clearer in recent studies than earlier ones in the waterbody environments. For example, the physico-chemical parameters, dissolved oxygen and metal distribution along a gradient of waterflow paths into Lake Victoria have been studied (Ochumba and Kabaara, 1989). Areas of metal input in river Papenkuils that was considered to be a serious source of pollution to the marine environment around Port Elizabeth have been identified (Watling and Emmerson, 1981).

In contrast, the estuary of River Swartkops in South Africa was found to be generally unpolluted on the basis of metal concentration in water, surface soils and soil cores (Watling and Watling, 1982). The concentrations of metals Pb, Cd, Se and As in water of the Winam Gulf, Lake Victoria, Kenya over the period of September 1997 to February 1998 have been determined and the spatial variability in various ranges of the elemental metals in the lake recorded. Further, it has been established that in most stations of Lake Victoria waters, metal concentrations are above the recommended values for drinking water (Tole and Shitsama, 2003).

2.3.3 Distribution of metals in soil media

Metals play an important role in the soil as nutrients to plants at low concentrations. Notwithstanding this, with long-term exposure of wastes containing metals, metallic concentrations can accumulate to phytotoxic levels and result in reduced plant growth and/or enhanced metal concentrations in plants, especially in low pH soils, which when consumed by animals then enter the food chain (Mbagwu *et al*., 2004). While it has generally been assumed that these metals are immobile in managed agricultural soils (Van Erp and Van Lune, 1991), some factors that enhance their mobility can result in more plant uptake or leaching of these metals to ground water. These factors include the properties of the metals, soil texture, pH and competing cations in the soil solution.

An extensive review of metal movement in soils shows that movement most likely occurred where disposal of sludge was made on sandy, acidic, low organic matter (OM) soils, receiving high rainfall or irrigation water (Dowdy and Volk, 1984). Evidence of

such movement in a sandy soil treated with sewage sludge at intervals over a period of 25 years has been shown (Smith, 1991). For instance, Cd retention was found to be greater in fine-textured soils with high cation exchange capacity (CEC) than in coarse-textured soils with lower CEC (Kuo *et al*., 1985). In general, metal mobility has been found to be closely associated with metal-organic complexation and soil pH. Also, metals added to the soil in wastes, particularly in sludge, accumulate on or very near to the surface layers of the soil (Van Erp and Van Lune, 1991). There is little other evidence to suggest that only a very small percentage of sludge-borne metals leach into the ground water if soil pH is maintained above 6.2 (Sidle and Kardos, 1977; Candelaria *et al*., 1995). After a 12-year disposal of sludge to soils, practically all the Zn, Cu and Pb were found to remain in the surface 0–20 cm of the soil (Anderson and Nielson, 1992). On the other hand, metals were observed to have moved down some 15 cm in soil following a 3- year disposal of sludge (Hinesley *et al*., 1972).

Although metal concentrations and distribution in soils have been studied extensively, there has been much contradictory evidence relating to metal mobility in soils. Data for Cu, Zn, and Pb distribution in soils as a result of long-term disposal of sewage sludge are more uncertain, particularly with respect to tropical ultisols. For example, it has been shown that the relative mobility of the more common metals in soils follows a typically trend of Zn > Cu > Pb (Elliot *et al*., 1986; Van Erp and Van Lune, 1991). However, in a 14-year study of sludge-amended soil, it was found that the concentrations of Cd and Zn in the leachate decreased over time, whereas Cu and Pb concentrations increased (Van Erp and Van Lune, 1991). There is therefore, need to review the information on the

distribution of metals in various soils around the world to understand the spatial variations in metals in soils of riverine environments.

There were no significant differences in Cd and Pb concentrations in soil among sites in the Persian Gulf. Concentrations of Ni and V in soils were, however, found to be significantly different from site to site (Pourang *et al.,* 2004). On the other hand, a study on distribution of adsorbed metals on the fine fraction of the soils of the western part of the Nile continental shelf showed that abundance of metals occurred in the order Fe > Zn > Cu, and that their distribution was identical with the pattern of soil transport (Wetzel, 2005). Distribution of Cu, Cd, Zn, Fe and Mn depicted a pattern similar to that of the mud and organic matter content of the soils (Saad *et al*., 1981). Statistical treatment of the results of metal analyses of 176 stream soil samples from the Ife-llesha area (1800 km^2) of Nigeria established that all the elements investigated had density distribution close to natural background levels (Ajayi and VanLoon, 1999).

Various statistical methods used for the interpretation of the geochemical data obtained from analyses of Cu, Pb, Zn, Co, Ni, Fe, Mg, Mn and Ca in 374 stream soil samples within the upper Benue Trough (Nigeria) established that these elements exhibit various patterns of association depending on their nature and prevailing environmental conditions (Ojo, 1988). In Côte d'Ivoire, metal concentrations in excess of background levels in soils of the Ebrié Lagoon were reported, with high variations in their spatial distributions discerned (Kouadio and Trefry, 2007). Also, anthropogenic metal enrichment of Cd, Co,

Cu, Cr, Fe, Mn, Ni, Pb and Zn in the Lagos lagoon was investigated and land based urban and industrial wastes sources implicated (Okoye *et al*., 1991).

Although available data on anthropogenic contaminants are scarce (Bryceson *et al*., 1990), localised hot spots of anthropogenic metal pollution are found in the vicinity of cities and industrial centres that may constitute a danger to public health. For example, slightly higher metal concentrations in water from Mombasa compared to Lake Victoria have been reported (Wandiga and Onyari, 1987). Soil samples near a battery factory in Dar-es-Salaam, Tanzania, were analyzed for mercury where the differences in distribution were associated with the disposal of defective batteries (Semu *et al*., 1986). A preliminary investigation of the extent of metal pollution of the Msimbazi River in Dar-es-Salaam, which receives industrial, urban and agricultural wastewaters, was conducted by analyzing soils and biological indicators (Akhabuhaya and Lodenius, 1988). Metal concentrations were in general low but some of the results indicated localized industrial pollution based on the concentration patterns of the metals.

Studies in Lake George and Lake Edward in Uganda, which included Cu and Fe in soils of the same rivers, concluded that the concentrations, although distinct in the different water bodies, did not show much variation within each of the rivers (Bugenyi, 1982). On the other hand, a study carried out to determine the degree of contamination of Kampala City, Uganda, by metals Zn, Cu, Pb, and Cd from industries and motor traffic showed that metal concentrations were highest in urban sampling sites compared to rural sites. However, it was recommended that the increased growth in industry and motor vehicle

traffic density in the city urgently calls for newer research to determine the current state of metal contamination of soils and crops grown around the city (Nyangababo, 1987).

In Kenya, soils in different parts of the country have been sampled for metal pollution (Greichus *et al*., 1978). Slightly elevated metal concentrations compared to earlier values found by Koeman *et al*., (1972) were reported. Metals Fe, Mn, Zn, Pb, Cu, Cr, Al and Cd in the less than 63 μm grain-size fraction in soils from selected rivers in Kenya have been studied (Mwamburi, 2003). In this study, temporal variations were significant for Zn, Cr and Pb. There were no significant longitudinal differences in all the elements in rivers Nyando, Nzoia, Yala and Sondu-Miriu, apart from soil Fe contents. Sampling for metals Cd, Cu, Fe and Zn content in soils at Port-Reitz Creek in Mombasa was carried out during July 1998. High values of Cu and Zn were observed near steel factory and crops-processing firms. Lateral distribution of Cd, Cu, Fe and Zn on surface soils showed a decline in concentration in a seaward direction (Kamau, 2002). Also, the levels of Cd and Pb in soils in Mombasa were studied between May 1997 and March 1998. The results established that Cd concentrations were generally below detection limits. Overall, Pb and Cd concentrations were low in the soils of Makupa and Tudor creeks, with a few incidents of elevated levels in metal concentrations especially during the rainy season (Mwashote, 2003).

2.3.4 Distribution of metals in sediment media

An important pathway of interaction between the organisms of aquatic ecosystems and their chemical environment is via what is contained in the aqueous phase (primarily in the

dissolved phase; but also to some extent in the particulate phase). However, the aqueous phase constantly undergoes chemical exchange with particulate matter in suspension and in the sediment bed; a number of these reactions can affect water quality. It is precisely these exchanges, and the chemical traces they leave in the sediment that are then preserved over time, that tell us the recent or past history of aquatic systems, and which provide useful insights into past geochemical, climatic and other conditions (Ondieki, 2006).

All metals exist in surface waters in colloidal, particulate, and dissolved phases, although dissolved concentrations are generally low. The colloidal and particulate metal may be found in bottom sediments. The behaviour of metals in natural waters is a function of the substrate sediment composition, the suspended sediment composition, and the water chemistry (Bryan, 1992). Sediments composed of fine sand and silt will generally have higher levels of adsorbed metals than will quartz, feldspar, and detrital carbonate-rich sediments. Metals also have a high affinity for humic acids, organo-clays, and oxides coated with organic matter.

A study on heavy metal content and lithogenical properties of sediments in the northern Adriatic reported that all metals investigated accumulated in the fine fraction ($< 63\mu m$) with the following percentages; Hg , 95% ; Zn, 68% ; Pb, 82% ; Cu, 79% ; Cd, 74% ; Ni, 70%, Cr, 65% ; Co, 65% and Fe, 64%. This phenomenon was attributable to the greater surface area for adsorption of matter on the finer grains (Donazzolo *et al*, 1984). Another study of bed soils from 23 stream sites representing various anthropogenic land uses in

the South Platte River Basin, USA in 1992 and 1993 established that concentrations of most metals in bed soils decreased with increasing distance from the mountains to the plains. In this study, As, Cd, Cu, Fe, Pb, Mn and Zn concentrations were highest in bed soils in mountainous mining areas. In the plains, concentrations of Al and Se were highest in urban land-use settings, whereas As, Cr, Ni and Ag were highest in mixed land-use settings (Heiny, 2002). Differences between natural and anthropogenic sources of Hg pollution in water have also been investigated by reviewing concentrations in pelagic crops and benthic organisms, as well as soils (Bernhard and Renzoni, 1977).

2.4 Anthropogenic contribution to the occurrence of metals

Anthropogenic activities play a major role in the introduction of various heavy metal pollutants into surface waters, resulting in elevated metal levels and lowered water quality. Point and non-point pollutant sources from industrial, urban waste discharges, runoffs, and agricultural leached chemicals coupled with the lithological characteristics are important factors modifying and influencing surface waters and sediments (Kalff, 2002).

Heavy metals enter the aquatic environment from both natural and anthropogenic sources. Entry may be as a result of direct discharges into aquatic ecosystems or through indirect routes such as dry and wet deposition and land runoff (WHO, 1996). Important natural sources are volcanic activity, continental weathering and forest fires. The contribution from volcanoes may occur as large but sporadic emissions due to explosive volcanic activity or as other low continuous emissions, including geothermal activity and

magma degassing (Manahan, 1992). The major sources of atmospheric Hg for example, are land degassing (GESAMP, 1988). In view of the toxic nature of the heavy metals, the knowledge of their sources and fate in the environment is important.

The anthropogenic sources include: mining effluents, industrial effluents, domestic effluents and urban storm-water run off, leaching of metals from garbage and solid waste dumps, metal inputs from rural areas, for instance metals contained in pesticides, atmospheric sources, such as burning of fossil fuels, incineration of wastes and industrial emissions (Zarazua *et al.,* 2006). In some African countries, mining activities are important sources of heavy metal input to the environment, for example mercury in Algeria, As in Namibia and South Africa, Sn in Nigeria and Democratic Republic of Congo and Cu in Zambia. For most heavy and toxic metals, anthropogenic emissions are more than or equal to natural emissions. The combustion of leaded petrol in automobiles, for instance, is responsible for the widespread distribution of lead in the world. For Hg, however, natural emissions are quantitatively more important than anthropogenic sources (Hutchinson and Meema, 2007; GESAMP, 1988).

Differential distribution of heavy metals from anthropogenic activities and natural processes are the responsible and shaping factors that determine the concentrations of metals through different pathways when they enter the environment. Increasing inputs from various treated or untreated municipal and industrial effluents, agricultural runoff or increased runoff due to the disturbance of drainage basins, as well as from the

atmosphere, threaten to alter quantitatively and qualitatively the natural biogeochemical cycles in many of the industrialized countries of the world (Kobingi *et al*., 2009).

2.5 Review of analytical Techniques

2.5.1 UV-Visible Spectrophotometer

2.5.1.1 General Basis of the Techniques

Absorption of light by one or more components of a solution is used to measure their concentration. Figure 2.1 below, the wavelength selector is a gelatin, glass or interference filter, whereas in more elaborate instruments a monochromator is employed, invariably now of the diffraction grating type (Hunt and Wilson, 1986). The detector in filter system is usually photocell, but photomultipliers are used in monochromator instruments. The read out on modern spectrophotometers normally consists of a digital display but many also have associated pen recorders.
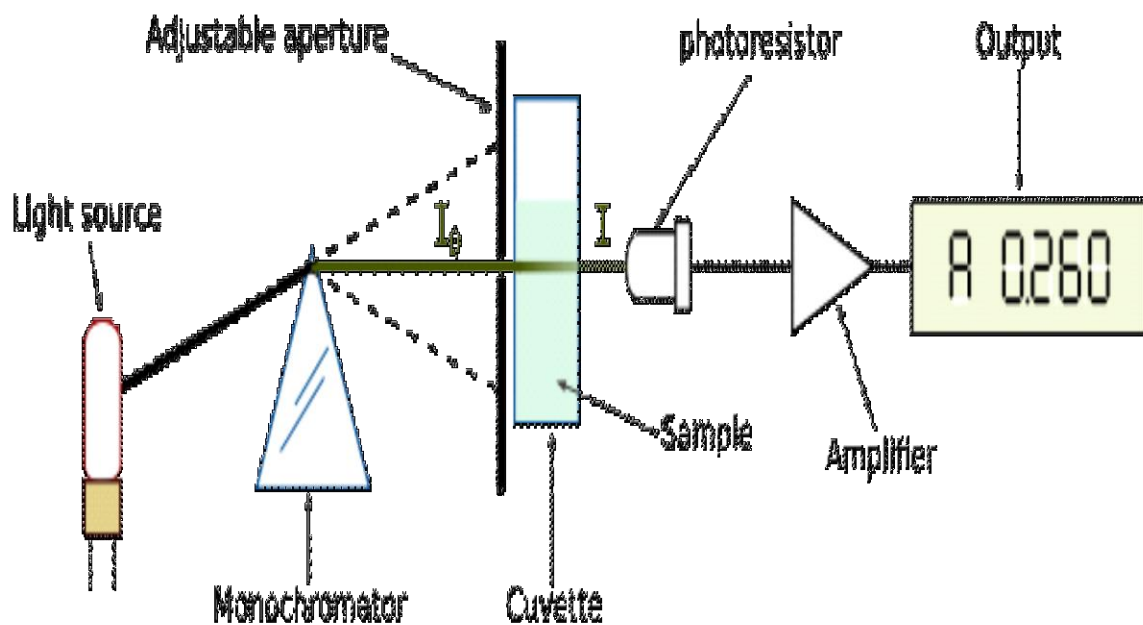
Figure 2.1: Schematic arrangements of typical instruments for spectrophotometer (Source: Hunt and Wilson, 1986).

It is usually necessary in spectrophotometer to add one or more reagents to the sample to convert the determinant into a strong absorbing substance. Familiar examples include the determination of nitrites by formation of a pink azo dye and the determination of chlorine using DPD (diethyl –P-Phenylene –diamine). Because so many chemical reagents and reactions can be exploited in solution spectrophotometer, the technique has wide applicability to both inorganic and organic substances. Spectrophotometer remains virtually essential to laboratories concerned with general water analysis particularly for the determination of the nutrients and elements (nitrogen, phosphorus and silicon) (APHA, 1992).

2.6 Atomic Absorption Spectrometry (AAS)

In analytical chemistry, atomic absorption spectroscopy is a technique used to determine the concentration of a specific element in a sample (Zybin, *et al.*, 2000). The technique can be used to analyze the concentration of over 70 different metals in a solution.

2.6.1 Principles

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample; it therefore, relies on the Beer- Lamberts law. The electrons of the atoms in the atomizer can be promoted to higher level for a short amount of time by absorbing a set quantity of energy. This amount of energy or wavelength is specific to a particular electron transition in particular elements and in general, each wavelength corresponds to only one element. This gives the technique its elemental selectivity.

As the quantity of energy (the power) put into the flame is known and the quantity remaining at the other side (at the detector) can be measured, it is possible from Beer- Lamberts law to calculate how many of these transitions took place, and thus gets a signal that is proportional to the concentration of the element being measured. It is therefore a versatile analytical technique in elemental analysis and comparable to the related techniques like flame emission spectroscopy (FES) and atomic fluorescence spectroscopy (AFS) (Godden, 1996).

2.6.2 Instrumentation

The main components of an AAS are as shown by the block diagram below (Figure 2.2).
In order to analyze a sample for its' atomic constituents it has to be atomized. The sample
is then illuminated by light. The light transmitted is finally measured by a detector. In
order to reduce the effect of emission from the atomizer or the environment, spectrometer
is normally used between the atomizer and the detector (Alkemade *et al*., 1982; L'vov,
1997; Broekaert, 1998 and Axner, 2000).
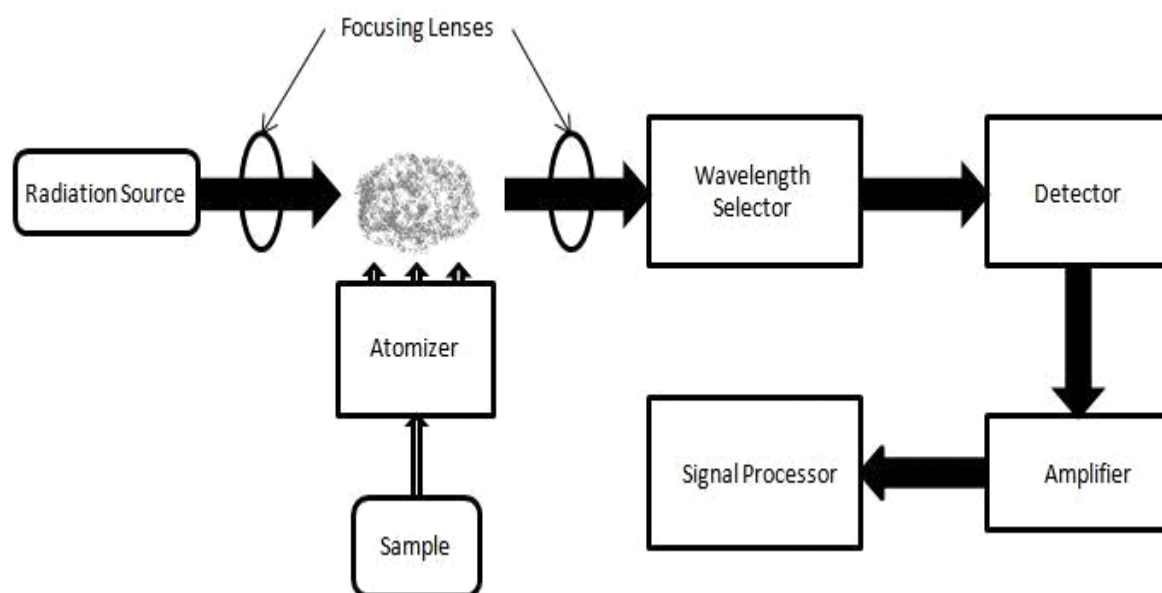
Figure 2.2: Block diagram of Atomic absorption spectroscopy (AAS) (Source: Zybin, *et al.*, 2000).

2.7 Olsen Method

The "Olsen P" or sodium bicarbonate soil test phosphorus (P) method was developed to predict crop response to fertilizer P inputs on calcareous soil. This method is based on the use of the HCO_3^-, CO_3^{2-} and OH^- in the pH 8.5, 0.5 M $NaHCO_3$ solution to decrease the solution concentrations of soluble calcium by precipitation as $CaCO_3$ and soluble Al^{3+} and Fe^{3+} by formation of Al and Fe oxyhydroxides, thus increasing P solubility. The increased surface negative charges and/or decreased number of sorption sites on Fe and Al oxide surfaces at high pH levels also enhance desorption of available P into solution (Olsen *et al.*, 1954).

CHAPTER THREE

3.0 MATERIALS AND EXPERIMENTAL METHODS

3.1 Chemical Reagents

Analytical grade reagents were used unless otherwise stated, these included; potassium iodide, hydrochloric acid, sodium thiosulphate, nitric acid, aluminum foil, buffer solution pH 4 , buffer solution pH 7.0, potassium manganate (VII), sulphuric (VI) acid, lead (IV) nitrate, chromium (II) nitrate, zinc Chloride, iron (II) chloride, ammonium molybdate, fiske reagents, sodium hydroxide, sulphalinic acid, brucine sulphate, chloroform, sodium chloride, potassium hydrogen phthalate, tris(hydroxyl methyl) amino methane, hexane, potassium nitrate, sodium bicarbonate, ascorbic acid, potassium antimony tartarate, salicylic acid, copper (II) nitrate, starch indicator and potassium dihydrogen phosphate. These chemicals were obtained from Sigma and Aldrich Company distributors in Kenya.

3.2 Equipment and Glassware

3.2.1 Glassware

Glassware used in the experimental method included; measuring cylinders, filter funnels, round bottomed flasks, beakers, wash bottles, volumetric flasks, graduated pipettes, burettes, BOD bottles, test tubes, stirring rod and thermometers

3.2.1.1 Cleaning of Glassware

Cleaning was done thoroughly to avoid the possibility of contamination; this was done by soaking the glassware in detergents and hot water overnight. It was then rinsed in plenty of hot water, rinsed again in distilled water and afterwards rinsed in hexane. The apparatus was then dried in an oven for at least two hours. Clean glassware was stored in separate labelled cabinets away from dust and possible contaminants before use.

Before sampling, the plastic sample bottles to be used were washed, soaked in dilute nitric acid overnight and rinsed thoroughly with distilled water. The bottles were also rinsed twice with river water at sampling sites before the samples were collected.

3.2.2 Analytical Balance

An electronic analytical balance was used in all measurements, weighing to four decimal places.

3.2.3 pH Meter

Measurements were done using pH meter (Jenway 370 model), calibrated using buffer solution, pH 4 prepared by adding 0.2 mL of 0.1M HCl to 100 mL of 0.1M potassium hydrogen phthalate. Buffer solution pH 7 was prepared by adding 93.2 mL of 0.1M HCl to 100 mL of tris (hydroxymethyl) amino methane.

3.2.4 Dissolved Oxygen Meter

Dissolved oxygen meter (Hanna model) was used to determine dissolved oxygen. The instrument was calibrated using potassium chloride solution.

3.2.5 Atomic Absorption Spectrophotometer (AAS)

AAS (CTA 2000 model) was used; a deuterium lamp was used for the automatic background correction of the signal. The burner height was adjusted to heights ranging from 6.0 -7.0 cm depending on the element being analyzed.

Air-acetylene mixture flame was used during the analysis. Cylinders of compressed acetylene of analytical grade were obtained from the British oxygen company (BOC) Kenya limited. Air was pumped by automatic air pumps to mix with acetylene during the analysis.

3.2.6 UV-Visible Spectroscopy

UV-Visible spectroscopy (C101-E100A shimamadzu model) was used; visible region 400-700nm and glass cuvettes were used during analysis.

3.2.7 Other Apparatus and Materials

These include: ovens, water distillers, plastic reagent bottles, crucible spatulas, cotton wool, stickers and whatman filter papers number 42, refrigerator, soil ogre, pestle, mortar and thermometer.

3.3 Sampling and Sample Preservation

3.3.1 Sampling locations

Four sampling sites were selected for this study based on the anthropogenic gradients of the catchments. The sites were S1, S2, S3 and S4 and their descriptions are as provided.

S_1; this was the remote point upstream Kapsabet River before the river enters the town. This point was expected to be the control point.

S_2; this was a point closer to Eldoret –Kapsabet route. It is an entry point of water into town.

S_3; this was a point where water leaves the town.

S4; this was a point which is approximately 1km downstream after the river water had left the town.

3.3.2   Sampling of Water

Fieldwork consisted of collecting water samples at four pre-determined sites at each of the sampling stations (Figure 1.1). These stations were at S1, S2 S3 and S4. The river water samples were obtained in duplicates using the Grab Technique using half litre metal free Van Dorn bottle. All water samples were drawn from about half metre (0.5 m) below the water surface at each of the two opposite sides of Kapsabet River. This depth was considered to represent a homogeneous water layer, free from riverbed sediment or atmospheric air interference. A total of 32 water samples were collected for this study. The samples were then transferred into pre-washed half litre polyethylene bottles. The bottles had been pre-washed by soaking in nitric and sulphuric acids solution of 1:1 volume ratio, washed in about 2 L of tap water and rinsed three times in distilled water and dried prior to field work. While in the field the sampling bottles were rinsed several times with river water. Water samples were acidified to pH 2 with concentrated nitric acid according to APHA (1998). This treatment was necessary so as to prevent loss of ions, which are normally adsorbed on the walls of the sampling container. After the preliminary treatment, the samples were placed into an ice box and transported to university of Eldoret laboratory for temporary storage in a refrigerator at 4°C before analysis.

3.3.3 Sampling of Sediments

Surface sediments were scooped from the bottom of Kapsabet River in duplicate using Ekmans Grab Sampler. The sediments were scooped from the four stations (S1, S2, S3 and S4). Sediment samples were taken from river bed positions where an accumulation of fine grained substrate occurred. The depth of water at each sediment-sampling site was measured using a metre rule. The wet sediment samples were kept separately in appropriately marked black polythene bags and transported to the University of Eldoret laboratory for chemical analyses.

3.3.4 Sampling of Soil

Within each of the four sites (S1, S2, S3 and S4) sampling points were established on a linearly transect towards the riverine farmland. This procedure was followed on both sides of the river. The river bank was taken as the reference (origin) point for both sides. An auger sampler was then used to scoop soil in duplicate at each sampling point. The soil was then kept in black polyethylene bags, labelled and then placed in an ice box and transported to the University of Eldoret laboratory for chemical analyses.

3.4 Determination of Temperature in Water

Water temperature was measured insitu using thermometer during sampling. Thermometer was immersed in the sample and the readings taken once it stabilizes.

3.5 Determination of pH in Water, Sediments and Soil

A pH meter was used to determine the pH of water. The pH meter, jenwey 370 model, was calibrated using buffer of pH 4 and 7. After calibration, the meter was immersed into the sample and results were recorded to one decimal place. After each measurement, the electrode was rinsed with distilled water.

Soil and sediment were dried in an oven for 12 hours at 30^0C. A 15 g of sample was measured into 50 mL beaker and 15 mL of distilled water added and stirred to mix completely. The pH meter was calibrated using buffer solution of pH 4 and pH 7. The electrode was then immersed into the solution when the pH meter stabilized and results recorded to one decimal place.

3.6 Determination of Total Suspended Solids (TSS)

Total suspended solids are the portion of solids that are retained by a filter of pore size 2.0 µm or smaller (ALPHA, 1992). A volume of 100 mL of water was filtered through Whatman GF/A glass fibre filter on a buncher funnel attached to a vacuum pump.

The filter papers were placed on glass petri dishes, dried in a hot box oven at temperatures of 103 °C -105 °C before and after filtration with cooling to room temperature in desiccators weighing until a constant mass was achieved. TSS was calculated from the difference between the mass of the filter paper after and before filtering divided by the sample volume (Hiner, 1972).

3.7 Determination of Total Dissolved Solids (TDS)

Total dissolved solids are those solids that pass through a filter with pore size 2.0 µm or less (APHA, 1992). A 25 mL of water was filtered through Whatman GF glass fibre filters on a buncher funnels attached to a vacuum pump. The filtrate was put in a pre-weighted pyrex beaker and evaporated in a gallen kamp hot box oven at a temperature of 103 -105 °C.

Samples were cooled in desiccators to room temperature and weighted returned into the oven for one hour, and then cooled in the desiccators to room temperature. This process was repeated until a constant mass was obtained.

The mass (B) of the beaker when empty and mass (A) of the beaker after drying were used to determine the total dissolved solid concentration (Hiner, 1972).

$$\text{TDS mg/l} = \frac{\{(A-B) \times 1000)\}}{\text{Volume of the samples}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\text{Equation 3.1}$$

3.8 Determination of Biochemical Oxygen Demand (BOD)

A 20 mL of sample was measured in situ and transferred to the BOD bottles. The initial oxygen reading was read using the DO meter. The solution was closed carefully not to trap in any air bubbles and then incubated in the water bath in an inverted manner. The temperature was maintained at 20°C. The solution was incubated for 5 days. After which the final oxygen reading was recorded. The BOD is given by the difference between the initial and the final readings (IBP, 1971).

3.9 Determination of Chemical Oxygen Demand (COD)

A 50 mL of the samples was added to 250 mL Erlenmeyer flask in triplicate. Two blanks of 50 mL double distilled water were used. A 50 mL of 0.02 M $KMnO_4$ was added to each flask and placed in a water bath at boiling point for one hour. Thereafter, samples were allowed to cool for 10 minutes and 5 ml of 10% KI was added followed by 10 mL of 2M H_2SO_4. Starch solution was used as an indicator during titration using sodium thiosulphate until the blue colour disappeared.

COD was calculated using the following equation

COD mg/L= $\dfrac{(a\text{-}b) \times m \times 1000}{c}$ …………………………Equation 3.2

where;

> a- Volume of thiosulphate for the blank.
>
> b- Volume of thiosulphate for the sample.
>
> c - Volume of sample
>
> m- Molarity of thiosulphate(1BP 1971)

3.10 Colorimetric Determination of Phosphates in Water

 The Fiske and Subbarow method was adapted for the colorimetric determination of available phosphate. A standard curve of PO_4^{3-} was prepared by diluting 0, 0.2, 0.4, 0.6, 0.8 and 1.0 ml of 100 ppm KH_2PO_4 measured into separate test tubes with 5.0, 4.8, 4.6, 4.4, 4.2 and 4.0 ml of distilled water, respectively. To each of the test tubes, was added 1.0 mL of 2.5M H_2SO_4 and then 1 mL ammonium molybdate solution. Finally 0.3 mL of

Fiske reagent (1.0 g of Fiske reagent in 6.3 mL distilled water) was added and mixed thoroughly and allowed to stand for deep blue colour to develop.

Optical density measurements were taken at 660 nm using uv-visible spectrophotometer (C101-E100A shimadzu model). A 1 mL each of the water samples and a blank was similarly treated without the standard. Standard curve was obtained by plotting the absorbance of standards run by the above procedure against concentration of standard solution. The phosphate concentration in the samples was determined using the corrected equation of the standard curve constructed (Fiske and Subbarow, 1925).

3.11 Colorimetric Determination of Nitrates in Water

This method is based upon the reaction of the nitrate ion with brucine sulphate in 6.5M H_2SO_4 solution at a temperature of 100 °C. The colour of the resulting complex was measured at 410 nm. To a mass of 1 g of brucine sulphate and 0.1 g of sulphanilic acid, 70 mL hot distilled water was added to dissolve followed by 3 mL conc. HCl. This was followed by cooling, mixing and diluting to 100 ml with distilled water and then stored in a dark bottle at 5 °C. This solution was stable for several months. A mass of 0.7218 g of anhydrous potassium nitrate (stock solution) was dissolved in distilled water and made up to 1 litre in a volumetric flask, then preserved with 2 ml chloroform per litre. In preparing standard solution, 10 mL of the stock solution was pipetted and made up to 100 mL in a volumetric flask. pH of the sample was adjusted to approximately 7 with 1M NaOH which was prepared by dissolving 40 g in distilled water and making upto 1 litre. The mixture was filtered to remove turbidity.

A standard curve of NO_3^- was prepared by diluting 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mL of stock solution (KNO_3), measured into separate test tubes with 5.0, 4.8, 4.6, 4.4, 4.2 and 4.0 mL of distilled water, respectively. A 10 mL of H_2SO_4 solution was added into each tube and mixed by swirling. After thermal equilibrium, 0.5 mL brucine sulphanilic acid reagent was added to each tube and carefully mixed by swirling, then placed in the test tube rack in water bath at 100^0C for exactly 25 minutes. It was then removed and immersed in the cold water bath and allowed to reach thermal equilibrium 20-25°C. 3mL of Samples and reagent blanks was also treated like the standard solutions. Absorbance was read, against reagent blank, using uv-visible spectrophotometer (C101-E100A shimamadzu model) at 410 nm using 1cm cells (Jenkins et al., 1964). Standard curve was obtained by plotting the absorbance of standards run by the above procedure against concentration of standard solutions. Determination of NO_3^- concentrations in the samples was done using the corrected equation of the standard curve constructed.

3.12 Determination of Phosphate in Soil and Sediments

3.12.1 Preparation of Reagents

Extracting solution

A 42 g commercial-grade $NaHCO_3$ was dissolved in distilled water and made to a final volume of 1 litre. Mixing of $NaHCO_3$ was done by heating the mixture and allowing it to cool. pH of the solution was adjusted to 8.5 with 50% sodium hydroxide.

1 M Sodium Hydroxide

This was prepared by weighing 10 g and dissolving in 200 mL water; the solution was cooled and filled to the mark using distilled water.

4% Ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O)$

A 20 g of ammonium molydate was dissolved in about 500 mL distilled water and stored in glass stoppered bottle.

2.5M Sulphuric acid

A 70 mL concentrated sulphuric acid was added into 400 mL distilled water in volumetric flask and the solution made to the mark and mixed thoroughly.

0.1M Ascorbic acid

A 1.76 g of the acid was dissolved in 100 mL of distilled water.

0.02M Potassium antimony tartrate $(KSbC_4H_4O_6)$

A 1.3715 g was dissolved in 100 mL of distilled water and diluted to the mark.

Colorimetric reagents

A 50 mL of 2.5 M sulphuric acid, 5 mL of potassium antimony tartrate, 15 mL of 4% ammonium molydate and 30 mL of 0.1M ascorbic acid, was mixed well after addition of each reagent.

A 4% ammonium molydate and potassium antimony tartrate reacts in acid medium with orthophosphate to form a heteropolyacid (phosphomolybdic acid) that was reduced to intensely coloured molybdenum blue colour by ascorbic acid (Murphy and Riley, 1962).

Procedures

A 8 g of dried soil or sediment was weighed and placed in Erlenmeyer flask. A 80 mL volume of extracting solution was added and shaken for 30 minutes using a shaker. Extracts were then filtered through Whatman No. 42 filter paper including a blank in each series.

Preparation of stock and standard solution

Stock solution was prepared by weighing 0.4391 g of dry potassium dihydrogen orthophosphate and dissolving in 500 mL distilled water then made to the 1 litre mark with distilled water and mixed well. A 20 ml of the standard stock solution was pipetted and diluted to 100 ml using extracting solution to make 20 ppm phosphate ions. 0, 2, 4, 6, 8 and 10 ml of standard solution were pipetted into 100 ml volumentric flasks and filled up to the mark with extracting solution. These solutions had concentration of 0, 0.4, 0.8, 1.2, 1.6, 2.0 ppm phosphate ions, respectively.

 A working standard curve of PO_4^{3-} was prepared by diluting 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mL of 100 ppm KH_2PO_4 measured into separate test tubes with 5.0, 4.8, 4.6, 4.4, 4.2 and 4.0 mL of distilled water, respectively. 8 ml of mixed reagent was added to each test tube. 0.5 ml of Sample extracts and blank were pipetted into 50 mL volumetric flask, 1 mL of 2.5 M sulphuric acid was added then mixed by swirling. A volume of 8 mL of the mixed

reagents was added, mixed and made to the mark using distilled water. After 20 minutes absorbance was read at 880nm using uv-visible spectrophotometer.

Concentration of PO_4^{3-} in sample = $\underline{(A-B) \times 1000}$ ……………………Equation 3.3
$\phantom{Concentration of PO_4^{3-} in sample = (A-B) \times 1000..........}$ W

Where: A; concentration of PO_4^{3-} in sample

B; concentration of PO_4^{3-} in the blank

W; weight of the sample

3.13 Colorimetric Determinations of Nitrates in Soil and Sediments

A 10 g of freshly sampled soil was placed into a plastic shaking bottle and 100 mL of 0.5M K_2SO_4 extracting solution added and shaken for an hour. Thereafter, the sample was filtered through No.42 whatman filter paper. A 1.6290 g of dry anhydrous potassium nitrate was weighed and diluted to 1litre in volumetric flask using distilled water; this stock solution had 100 ppm NO_3^-.

The standard solution was prepared by diluting 0, 0.2, 0.4, 0.6, 0.8 and 1.0 mL of 100 ppm potassium nitrate into separate test tubes with 5.0, 4.8, 4.6, 4.4, 4.2 and 4.0 mL of distilled water, respectively..

A 0.5 mL of each sample, blank and standard were pipetted into labelled test tubes and 1.0 mL salicylic acid added and mixed well and left for approximately 30 minutes. A 10 ml of NaOH solution was added to each labelled test tube and left for an hour for yellow colour development. Absorbance was read at 410 nm using uv-visible spectrophotometer. From the graph of working standards of NO_3^-, the concentration of each unknown and the blank was determined. The corrected concentration was obtained as follows;

NO_3^- N (ppm soil) = $\underline{C \times V \times MCF \times 1000}$ ………………………Equation 3.4
 W

Where: C; corrected concentration, obtained by subtracting the mean blank values from the unknown

V; extraction volume

W; weight of sample (soil or sediment) in g

MCF; Moisture correction factor

3.14 Wet Digestion of Samples for Determination of Heavy Metals

3.14.1 Soils and Sediments

Wet oxidation, which is normally carried out by digesting samples in mixtures of concentrated nitric acid and sulphuric acid of 1:1 v/v ratio (FAO, 1975; Han *et al*., 1994) was used to digest the soils and sediments collected from Kapsabet River. A portion of the soils and sediments from each site was put into different crucibles. Each of these crucibles had been dried in an oven and pre-weighed. The soils and sediment samples were separately placed in the oven and dried at 105 °C for 24 hours (Han *et al*., 1994).

A sub-sample of the cooled soil and sediment were homogenized and sieved. Two grams of each set of the sieved soil sediment was then digested for one hour on a hot plate. 2 ml of 30% H_2O_2 was added to cooled samples and warmed to complete the digestion. The samples were cooled again to room temperature, filtered using 0.45 µm nucleopore filters. The volume of the resultant filtrate was made up to 50 ml mark in conical flask with deionized water. The filtrate was analyzed for the four metals in the same way as in the case of the water samples. The readings of the concentration of metals in the sample materials were done using AAS (CTA 2000 model).

3.14.2 Water Samples

Water samples were digested as a pre-requirement for spectrophotometer analysis so as to avoid interference from complexing organic matter (FAO, 1975). A combination of sulphuric acid and nitric acid digestion was used in this study (APHA, 1998). Samples were digested and concentrated on a hot plate from 100 ml to 25 ml for 3 hours. After digestion, the samples were cooled and 2 ml of 30% H_2O_2 was added to each sample to oxidize any resistant organic matter (Reynolds and Thompson, 1970; Onyari *et al.*, 1991). After cooling to room temperature the digested samples were filtered into 125 mL polyethylene bottles through 0.45 μm nucleopore filter paper over a vacuum pump. The concentration of metals in a sample was determined by an AAS (CTA 2000 model). Prior to reading of the concentration of metals in the samples, at least two calibration standards were prepared for each metal. Each blank consisted of a mixture of 10 mL nitric acid, 10 mL sulphuric acid, 2 mL of 30% H_2O_2 and 25 mL of distilled water.

3.14.3 Determination of Heavy Metals in Soil, Sediments and Water

3.14.3.1 Preparation of Stock and Working Solutions

Lead stock solution and working solution

A stock of lead was prepared by dissolving 1.599 g of lead (II) nitrate in nitric acid and making it to 1000 cm^3. This solution was equivalent to 1000 ppm lead ions. A stock solution of 100 ppm was prepared by pipetting 10.0 cm^3 from 1000 ppm stock solution,

putting it in 100 cm^3 volumetric flask and making it up to the mark with deionized water. Standard solutions of 2.5 ppm, 5.0 ppm, 7.5 ppm, 10.0 ppm were prepared from stock solution.

Iron stock and working solution

Iron standard stock solution was prepared by dissolving 4.244 g of iron (II) chloride (FeCl$_2$.6H$_2$O) in 12% hydrochloric acid and making the solution to one litre. The resulting solution had a density of 1.01 g/ml. and containing 1000 ppm of Fe (II) ions. A stock solution of 100 ppm was prepared by pipeting 10.0 cm^3 from 1000 ppm stock solution, transferring it in 100.0 cm^3 volumetric flasks and making it up to the mark with deionized water. Iron standard solution of 2.0 ppm, 4.0 ppm, 6.0 ppm and 8.0 ppm was prepared from the stock solution.

Zinc stock and working solution

Zinc standard stock solution was prepared by dissolving 2.116 g of ZnCl$_2$) in 12% hydrochloric acid and making the solution to one litre. Resulting solution had a concentration of 1000 ppm of Zn (II) ions. A stock solution of 100 ppm was prepared by pipeting 10.0 cm^3 from 1000 ppm stock solution, putting it in 100.0 cm^3 volumetric flask and making it up to the mark with deionized water. Zinc standard solution of 0.4 ppm, 0.8 ppm, 1.2 ppm, 1.6 ppm and 2.0 ppm were prepared from the stock solution.

Copper stock and working solution

This was prepared by dissolving 3.802 g of Cu(NO$_3$)$_2$.3H$_2$O in 12% nitric acid and making the solution to one litre. This solution was equivalent to 1000 ppm of Cu ions. In

order to make a solution of 100 ppm, 10 ml of the solution was pipetted and made to the 100 cm^3 mark in volumetric flask. Copper standards of 1.0 ppm, 2.0 ppm, 3.0 ppm, 4.0 ppm, 5.0 ppm, 6.0 ppm and 7.0 ppm were prepared from the stock solution.

3.14.4 Data Analysis

All data collected were entered, organized and managed using EXCEL spreadsheet for Windows XP. Results obtained were subjected to apriori test to determine the homoscedasticity (Michael and Douglas, 2004) before subjecting them to statistical analysis. The normality of the data distribution was checked by means of skewness and Kurtosis when performing analysis of variance. However, before conducting t-test, Levene's test on homogeneity of variance was conducted.

Data on the heavy metals, Pb, Zn, Cu, and Fe in water, soils and sediments were calculated as means (± S.D) for each site on each sampling occasion. Mean differences in the heavy metals among sites were analyzed using a one-way ANOVA; the differences between dry and wet seasons being analyzed by student t-test. Spatial variations in heavy metals concentration was examined by Two-Way ANOVA. Where significant differences were discerned among attributes analyzed by ANOVA, Duncans Multiples Range test (DMRT) was used to discriminate between the means (Michael and Douglas, 2004).

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Spatial and temporal changes in the physico-chemical parameters (pH, BOD, COD, TSS and TDS levels) in water of Kapsabet River

The results of the spatial variation of Kapsabet River's water physico-chemical parameters measured in all the four sampling sites over the study period are presented in Table 4.1

Table 4.1: Spatial mean values (± SD) of the physico-chemical parameters in four sites of Kapsabet River water.

Parameters	Sampling sites				Statistical analysis	
	S1	S2	S3	S4	F	p-value
pH	7.91 ± 0.71^a	9.79 ± 0.14^c	9.06 ± 0.52^b	8.88 ± 0.67^b	24.551	0.0002
TSS (mg/L)	355 ± 90.4^a	590.5 ± 82.1^b	627.5 ± 101.1^b	730 ± 89.7^c	13.224	0.0211
TDS (mg/L)	2456 ± 293^c	2147 ± 318^b	2062 ± 272^b	1613 ± 363^a	19.112	0.0012
COD	29.2 ± 6.5^a	26.7 ± 9.4^a	35 ± 7.2^b	44.0 ± 9.7^c	9.433	0.0431
BOD	5.2 ± 3.2^a	10.7 ± 3.1^b	12.5 ± 3.6^c	18.5 ± 4.2^d	25.675	0.0000
Temp (^{0}C)	19.5 ± 0.8	20 ± 0.6	20.1 ± 0.5	20.5 ± 0.3	2.113	0.0971

Similar lettering across the row represents concentrations that do not differ significantly ($p > 0.05$) based on one-way ANOVA test followed by post-hoc Duncan's Multiple Range Test.

 Results of the one-way analysis of variance (ANOVA) performed on the data related to pH, TSS, TDS, COD and BOD suggested that all the measured parameters except

temperature varied significantly among the sites (Type III, One-Way ANOVA; p < 0.05). The ranges of most of the physico-chemical parameters were within normal ranges of fresh water with some deviations. Generally, a pH range of 7.1 to 8.0 is considered pristine environment.

 In the current study, the pH ranged from 7.91 to 9.79, as shown in Table 4.1 which was above the WHO standard limits of 6.5-8.5. This indicates alkaline conditions reminiscent of external inputs of alkaline substances into the aquatic environment. The state of neutral to alkaline pH values obtained in the sampling sites were similar to those reported elsewhere (Morrison *et al*., 2001). Post-hoc analysis using Duncan's Multiple Range Test (DMRT) indicated that site S_1 had the lowest pH (7.91) probably because of its undisturbed environment and had near neutral pH. Point S2 had the highest pH (9.79) and this could be due to the site being near the Eldoret- Kapsabet bridge. Further, People bath in this area while others conduct the business of washing motor cycles and cars in it. TSS was significantly higher at site S_4 (730 ± 89.7 mg/L); this could be attributed to the dissolution of substances from the nearby Kapsabet town as was reported in earlier studies for areas situated near urban centres (Raburu, 2003).

The input of substances into the water bodies can be confirmed by high concentrations of TDS in the water ranging from 1613-2456 mg/L, which are higher than those reported in river Nyando of 110.1-142 mg/L (Raburu *et al*., 2011). However, the amount of TDS was significantly higher at S1 (2456 ± 293 mg/L) which can be associated with discharge of large amount of allochthonous materials in water from the decomposing litter in the forest. Both TSS and TDS had limits higher than WHO of 30 mg/L and 500 mg/L,

respectively. Elevated TDS can be toxic to freshwater animals by causing stress and affecting osmorequlatory capability of the organism (McCulloch *et al*., 1993). The concentration of COD and BOD were highest at site S4, which could be attributed to the presence of large number of organic substances such as humic substances that decompose and therefore consuming a lot of oxygen from the water column (Braide *et al.,* 2004). This could also be due to the high level of chemical species present in the agricultural effluent from tea farms, which demands high level of oxygen for oxidation of organic matter by a strong chemical, hence increasing COD levels. COD and BOD were within the WHO maximum allowable limits of 250 mg/L and 20 mg/L, respectively. Temperature did not exhibit any significant spatial differences since there were no major sources of discharge likely to elevate the water temperature.

Generally, the water flow in Kapsabet River starts from the upstream before Kapsabet town, and then flows towards river Yala which flows into Lake Victoria. Under normal hydrological flow regime, it is normally expected that a defined gradient of temperature, pH, TSS, TDS, COD and BOD would be obtained defined by downstream flows from the rithron to the potamon (Wetzel, 2001, Kalff, 2002; Luoma and Rainbow, 2008). However, when there are deviations with sudden decline and increase of these nutrients then, it is normally an indication of inputs from external sources.

The temporal mean values of the physico-chemical parameters are summarized in Table 4.2. Significant seasonal differences in the concentration of the measured parameters in water were observed (*t*-test for all parameters; $p < 0.005$). All parameters tested were found to be significantly higher in the rainy season than the dry season. Although rains

are supposed to bring dilution effects into the water body (Wetzel, 2005), the exceptionally higher pH during rainy seasons indicates presence of external inputs of substances that affect the levels of pH in the water. This suggest ability of runoff water to carry with it many different substances

Table 4.2: Temporal mean values (± SD) of the physico-chemical parameters in dry and rainy season of Kapsabet River water.

Parameters	Season		Statistical analysis	
	Dry	Rainy	*F*	p-value
Ph	8.14 ± 0.33^a	9.68 ± 0.31^b	24.551	0.0002
TSS (mg/L)	145.0 ± 14.4^a	956.3 ± 98.8^b	13.224	0.0211
TDS (mg/L)	1537 ± 134^a	2602 ± 107^b	23.105	0.0011
COD (mg/L)	9.81 ± 1.05^a	51.63 ± 3.64^b	17.411	0.0033
BOD (mg/L)	4.25 ± 0.32^a	23.25 ± 2.1^b	54.675	0.0000
Temperature (^{0}C)	19.8 ± 0.3	18.8 ± 0.4	12.113	0.0071

Similar lettering a cross the row represents concentrations that do not differ significantly

(p > 0.05) based on t-test

The spatial and temporal variations in the values of the various physico-chemical parameters determined in the four sampling sites along Kapsabet River are presented in Table 4.3. There were significant spatial and temporal variations in the levels of measured physico-chemical parameters in water (Two-Way ANOVA; $p < 0.05$). That means that seasons and sites of occurrence were main factors that determined the concentration of the measured parameters suggesting that rain and presence of human factors   contributed   to   the   occurrence   of   these   substances   in   water.

Table 4.3: Spatial and temporal mean values (±SD) of the physico-chemical parameters in four sites during dry and rainy season of Kapsabet River water.

Parameters	Sampling sites								Statistical analysis	
	S1		S2		S3		S4		F	p-value
	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy		
pH	7.3 ± 0.1	8.7 ± 1.1	9.6 ± 0.1	10.0 ± 0.5	8.2 ± 0.1	9.9 ± 0.1	7.7 ± 0.1	10.1 ± 0.2	19.22	0.017
TSS (mg/L)	135 ± 41	575 ± 45	130 ± 20	1050 ± 142	155 ± 15	1100 ± 100	160 ± 11	1100 ± 201	83.99	0.000
TDS (mg/L)	1950 ± 50	2962 ± 38	1600 ± 120	2695 ± 423	1600 ± 125	2525 ± 345	1000 ± 132	2225 ± 432	78.11	0.000
COD (mg/L)	6.5 ± 0.5	61.5 ± 5.5	9.5 ± 0.8	44.1 ± 4.2	14.2 ± 0.6	52.3 ± 5.3	9.4 ± 1.1	49.5 ± 12.3	29.43	0.000
BOD (mg/L)	3.5 ± 0.5	27.5 ±5.2	4.5 ± 2.1	20.5 ± 3.8	5.5 ± 0.9	24.6 ± 3.8	3.5 ± 0.5	21.7 ± 4.4	87.67	0.000
Temp (^{0}C)	19.5 ± 0.5	17.5 ± 0.5	20.5 ± 0.7	19.5 ± 0.4	20.8 ± 0.9	20.9 ± 1.8	19.0 ± 2.1	18.5 ± 1.1	22.11	0.008

4.2 Spatial and temporal variation in the levels of selected nutrients in water, soils and sediments of Kapsabet River

4.2.1 Dynamics of phosphates in Kapsabet River.

The spatial concentration of phosphates in water, soils and sediments at the four sampling sites of River Kapsabet is shown in Figure 4.1.
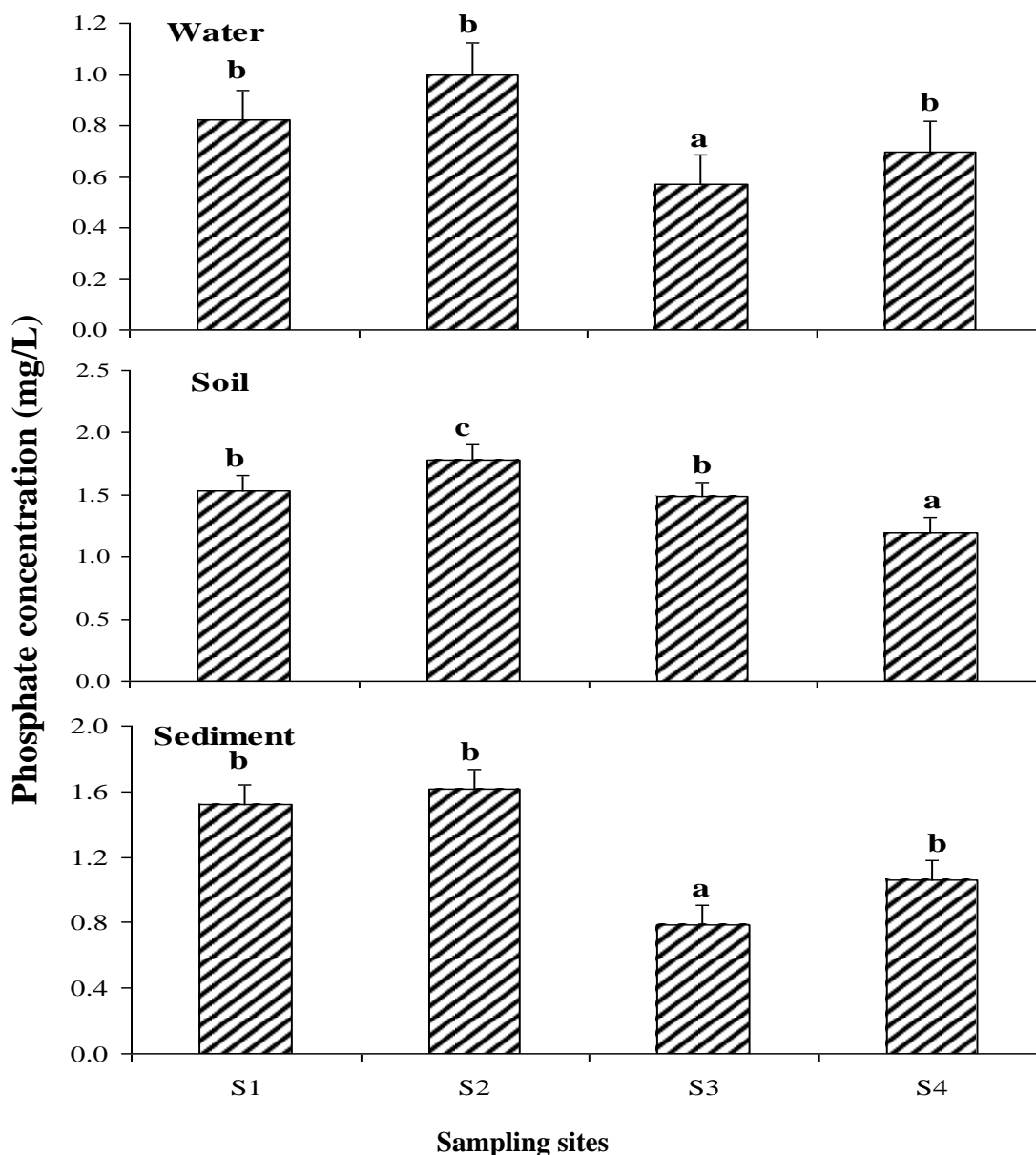
Figure 4.1: Spatial values of phosphates along the four sampling sites in water, soils and sediment of Kapsabet River (Source: Author, 2012).
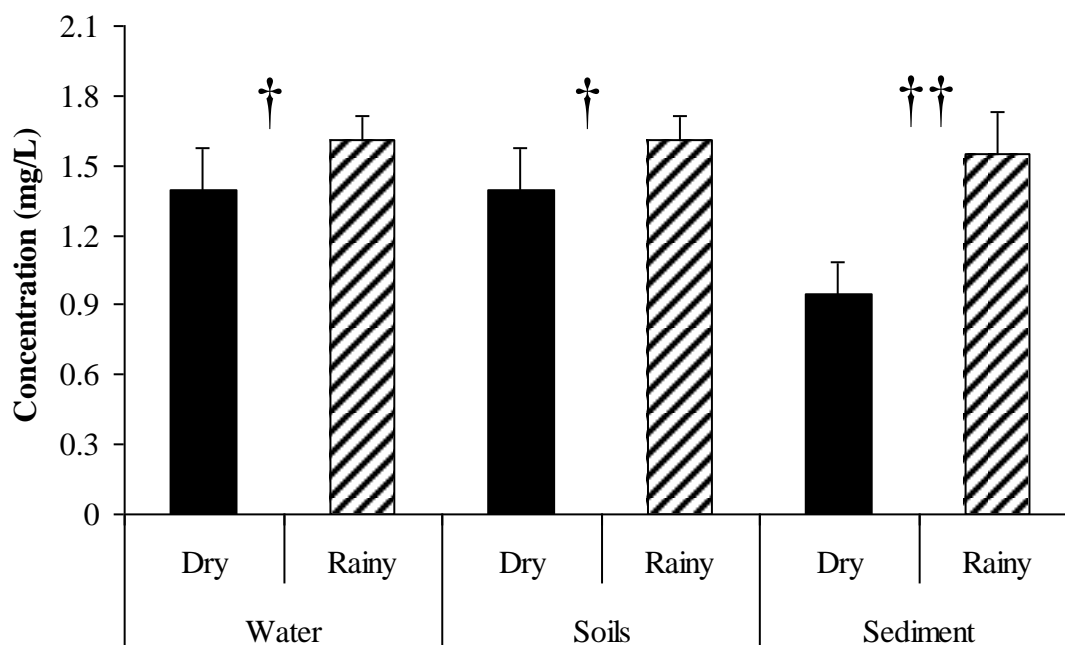
Similar lettering across each sample graph represents concentrations that do not differ significantly (p > 0.05) based on t-test.

Significant differences were observed in the concentrations of phosphate among sites in water, sediments and soils (One-Way ANOVA; $p < 0.05$). It was also discerned that there were significant relationships between phosphates in water, soils and sediments. The highest concentration of phosphates occurred at site S2 in all the analyzed media and lowest at site S_3 in water and sediments and site S4 in the soils. The direct relationships between phosphates levels in water and sediments was expected since phosphates in water normally settle to the sediments and may be re-mobilized during times of the river mixing regime (Kalff, 2002). Therefore, it appears that there could be heavy use of compounds of phosphorus that elevated the concentration of phosphates in soils at site S2. The phosphates were taken into the water body through overland flow and then accumulated in the bottom of the river sediments. A casual survey of site S2 indicates that there is a likelihood of extensive use of fertilizers in this area than in other sites such as S1, which has lower agricultural activities. Again, most of the washing points along the river are located in this site and therefore likely to elevate the levels of phosphates in water. However, site S2 had lower elevations than other sites and therefore likely to receive a lot of non-point sources of inputs from other watershed into the water body, which is likely to elevate the amount of phosphates in the sampling site. All the four sites show that water in this river exceeded WHO maximum allowable limit of 0.1 mg/L.

The temporal mean concentration of phosphates in water, soils and sediments at the four sampling sites of River Kapsabet during the rainy and dry is shown in Figure 4.2. Rainy season resulted in significantly higher concentration of phosphates in all the environmental media because of the possible input of phosphates from the external

environment into the river. Previous studies have established that phosphates are usually highly adsorbed into the soil and can be transported from the upper parts of the river catchments into the recipient water bodies and may account for the high phosphates concentration in local water bodies even if there are no evident point sources of pollution (Wetzel, 2005).

Figure 4.2: Temporal mean values of phosphates in dry and rainy seasons in water, soils and sediments of Kapsabet River (Source: Author, 2012).

Similar pattern across each graph represents concentrations that do not differ significantly (p > 0.05) based on t-test.

The spatial and temporal variations of phosphates among the four sampling sites are shown in Figure 4.3. There were significant spatial and temporal variations (ANOVA; p < 0.05) in the concentration of phosphates in water, soils and sediments with the wet season having highest levels in all the media. In water, highest concentration of phosphates was recorded in site S2 followed by S1 during the rainy season while in dry

season the highest level was in site S1. In the soils, highest phosphates concentration occurred at site S1 during both the dry and rainy seasons while in sediments, sites S1 and S2 had the highest amounts in dry and rainy season with no discernable significant differences in seasons at site S3.
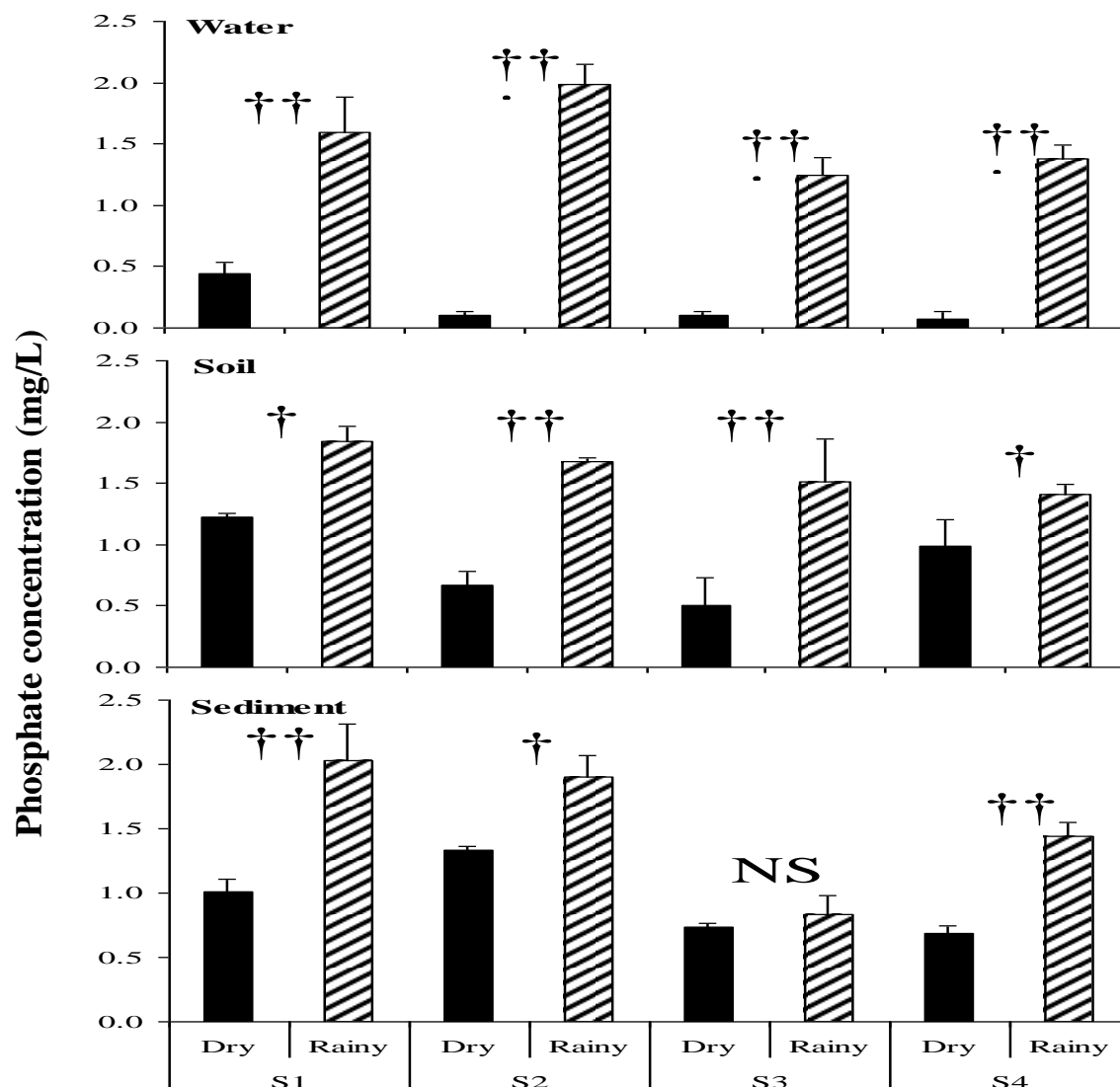
Figure 4.3: spatial and temporal concentration of Phosphates in the four sites in dry and rainy season in water, soils and sediment of Kapsabet River (Source: Author, 2012).

Similar pattern a cross each graph represents concentrations that do not differ significantly (p > 0.05) based on t-test

NS: No significant difference.

These results indicate that at each site, there was relative contribution of external sources of phosphates which could not be easily detected in the surrounding riparian ecotones. This could possibly be due to overland flow and soil sediment transportation from the upper parts of the catchments. S2 receives run offs from Chepterit market in addition to contribution from washing of vehicles and people bathing there. All these activities contribute to elevated levels of phosphate in this site besides agricultural activities along the sides of the slope. The results obtained in this study correlated well with the ones obtained in Keiskamma River (0.03-2 mg/L) (Morrison et al., 2001).

4.2.2 Dynamics of nitrates in Kapsabet River

The spatial concentration of nitrates in water, soils and sediment at the four sampling sites of River Kapsabet is shown in Figure 4.4. Significant differences were observed in the concentration of nitrates among the four sites in water, sediments and soils as presented in Figure 4.4 (One-Way ANOVA; $p < 0.05$). Results show that, concentration of nitrates increased significantly from site S1 to site S4 systematically. S3 had the highest concentration of nitrates and this can be attributed to extensive farming which takes place in the vicinity. This could be confirmed by high concentration of nitrates in the soil. There is a direct relationship between nitrates in water and sediments since the nitrates in water normally leach to the sediments and may be re-mobilized during times of the river mixing regime (Liu *et al.,* 2005).Therefore, it appears that there is heavy use of nitrogenous fertilizers in the farms and additional inputs from the nearby urban centres resulted in elevated levels of nitrates in water and subsequent transference to the sediments. Again due to the small nature of the river, most of the nitrogenous fertilizers

will have very strong influence on the nutrient status of the river and likely to elevate the

concentration of nitrates in water
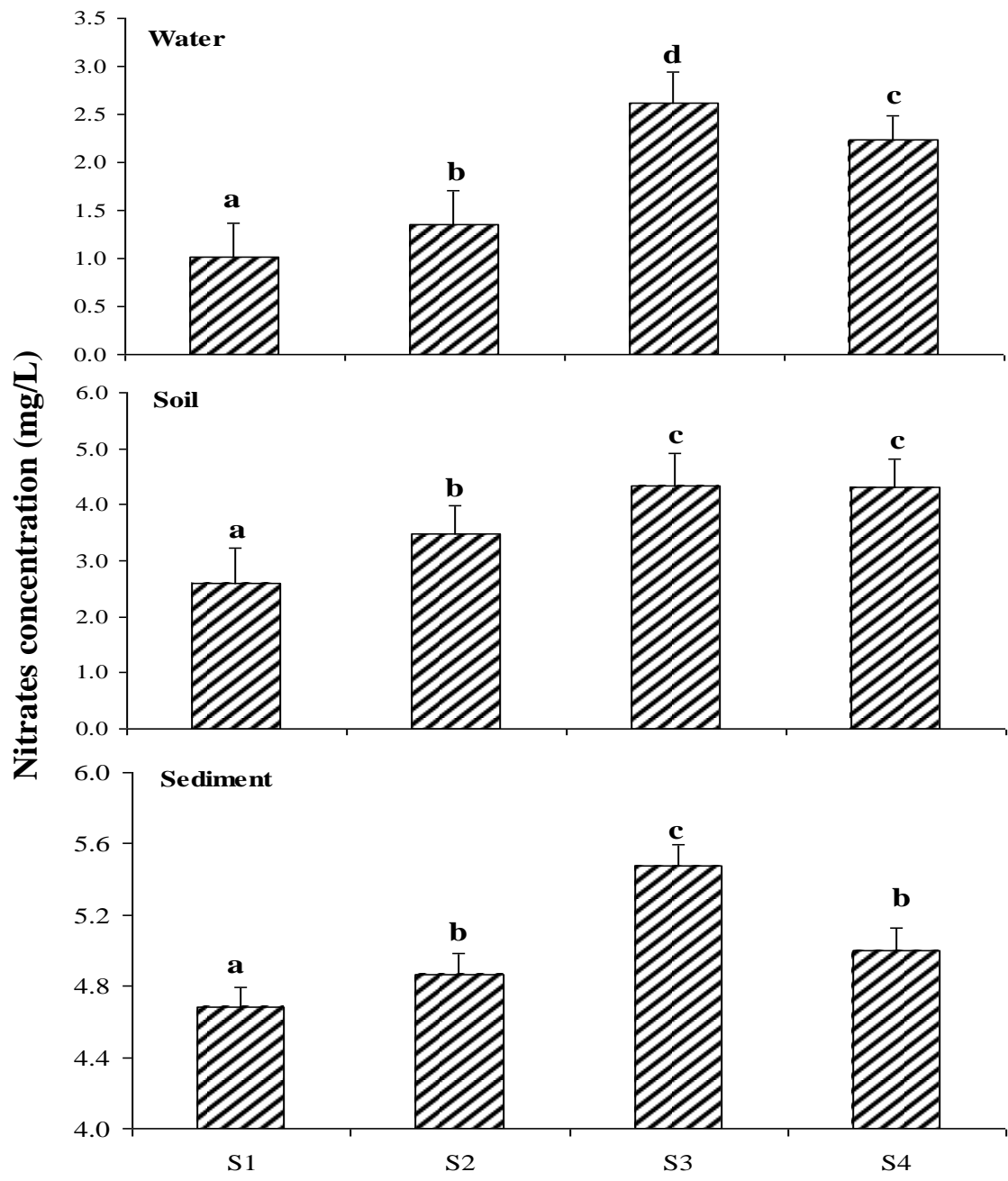
Figure 4.4: Spatial concentration of nitrates along the four sampling sites in water, soils and sediment of Kapsabet River (Source: Author, 2012).
Similar lettering a cross each graph represents concentrations that do not differ significantly (p > 0.05) based on t-test.

The temporal concentration of nitrates in water, soils and sediments at the four sampling sites of River Kapsabet during the rainy and dry seasons is shown in Figure 4.5.
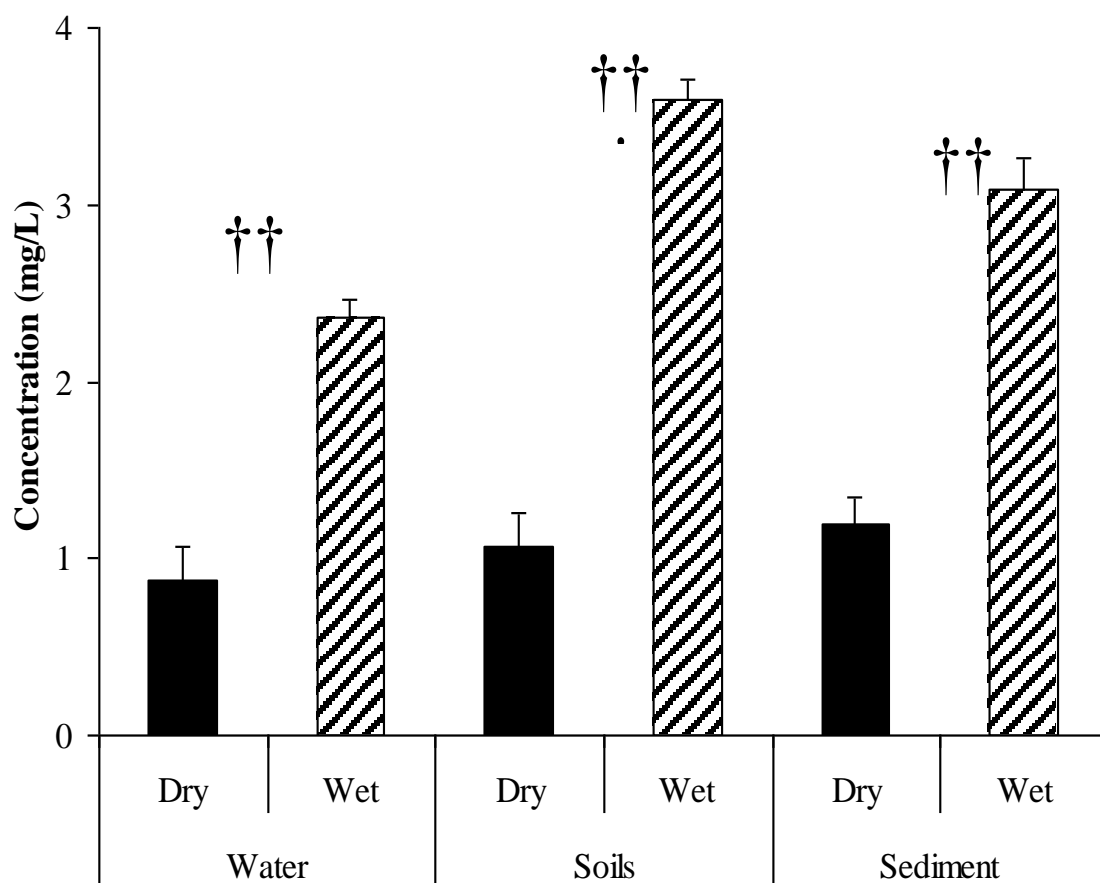
Figure 4.5: Temporal concentration of nitrates along the four sampling sites in water, soils and sediment of Kapsabet River (Source: Author, 2012).

Similar patterns represents concentrations that do not differ significantly ($p > 0.05$) based on t-test

Rainy season resulted in significantly higher concentration of nitrates in all the environmental media because of the possible input of nitrates from the external environment into the river. Statistical analysis of the results comparing the respective mean levels of nitrates for the dry and wet seasons showed a marked significant difference ($p < 0.05$), with highest mean level occurring in the wet season. This could be explained from the wash offs containing these nutrients from the catchments area into the river. The high level of nitrates in the soil during rainy season is an indication of the high use of this nutrient in crop production.

The spatial and temporal variations of nitrates among the four sampling sites are shown in Figure 4.6. There were significant spatial and temporal variations (ANOVA; $p < 0.05$) in the concentration of nitrates in water, soil and sediments with wet season having the highest concentration of nitrates in all the media. In the three media, there was a systematic increase in the concentration of nitrates along the sites from S1 to S4 during both the dry and rainy seasons. There was a systematic increase in the concentration of nitrates in water attributed to increased inputs of external contaminants into the water body from both agricultural and Kapsabet municipal centre. These results also signify that at each site, there was relative contribution of external sources of nitrates that could not be easily detected in the surrounding riparian ecotones and could possibly be due to overland flow and soil sediment transportation from the upper parts of the catchments.
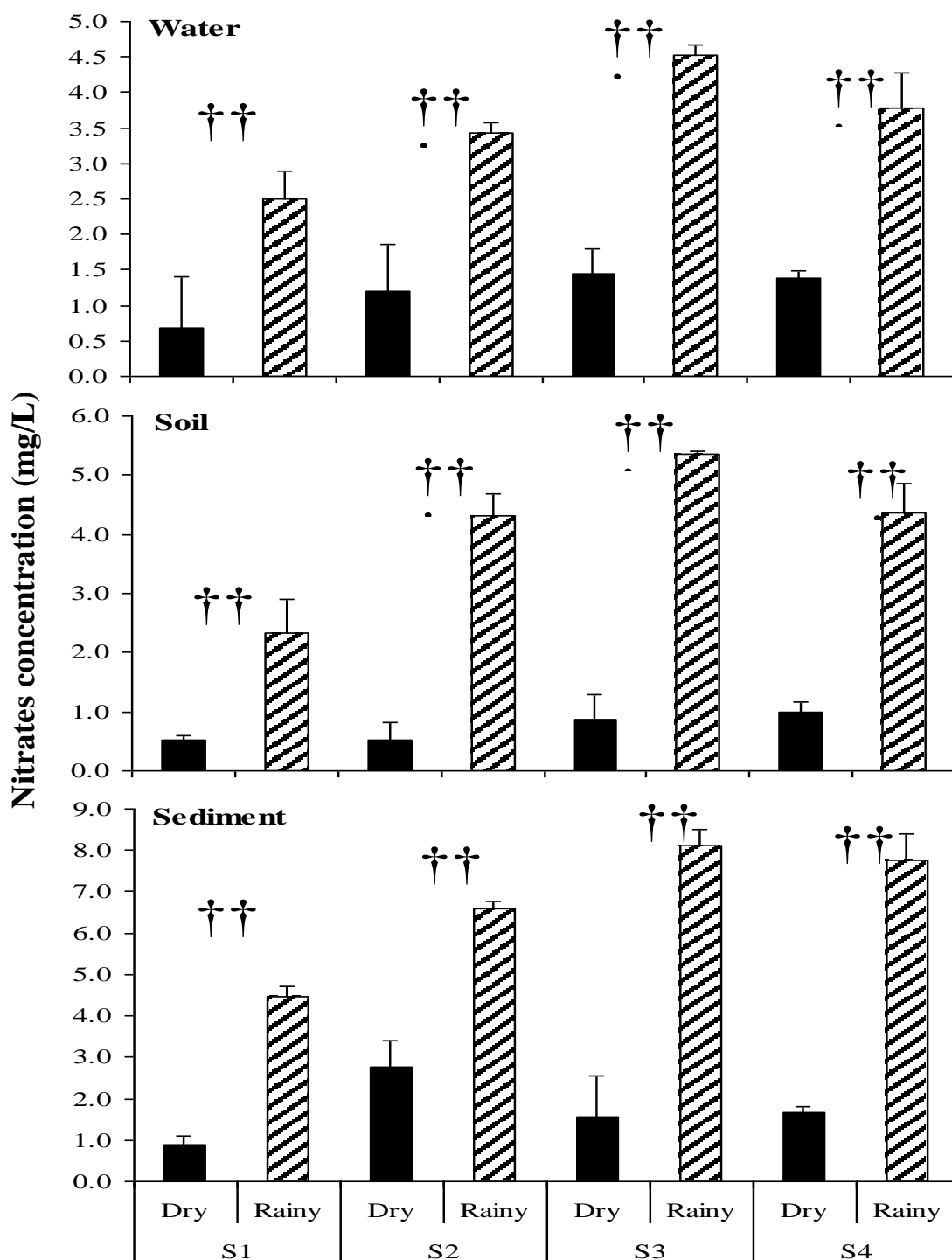
Figure 4.6: Spatial and temporal values of the nitrates in the four sites during dry and rainy seasons in water, soils and sediment of Kapsabet River (Source: Author, 2012).
Similar pattern across each sample graph represents concentrations that do not differ

significantly (p > 0.05) based on t-test

4.3 Spatial and temporal changes in the levels of heavy metals in water, soil and sediments of Kapsabet River

4.3.1 Spatial variation in metal distribution in Kapsabet River(water, soil and sediments)

4.3.1.1 Spatial variation in metal distribution in water of Kapsabet River

The spatial results of metal concentrations in water of Kapsabet River during the study period are shown in Figure 4.7.

Figure 4.7: Spatial concentration of metals in water at the four sampling stations during the study period in River Kapsabet (Source: Author, 2012).

Similar lettering a cross each graph represents concentrations that do not differ significantly (p > 0.05) based on t-test
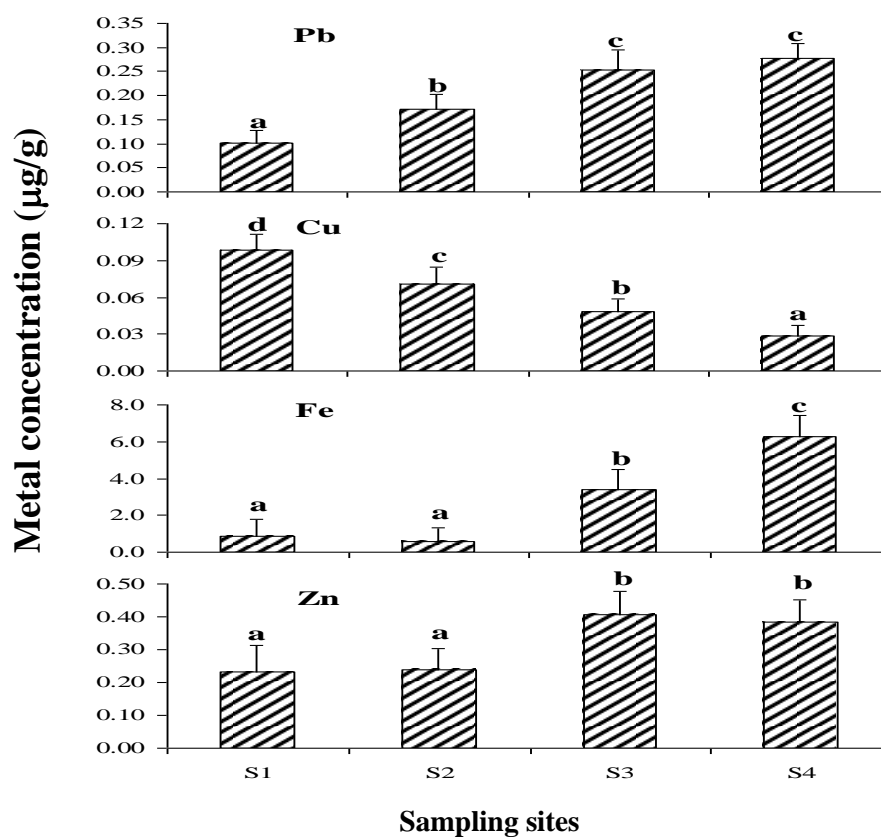
Spatial distribution of heavy metals in the water showed consistent patterns of variations for all the metals among the four stations. All the four metals investigated displayed significant differences ($p < 0.05$) among the sampling station. Concentration of Pb, Fe and Zn increased along the river profile to the highest in sites S3 and S4. However, the concentration of Cu tended to decrease from upstream to downstream. The high concentration of Pb, Fe and Zn in sites S_3 and S_4, which are all located near Kapsabet Town could be attributed to the runoffs, industrial discharge of Chebut tea industry, in addition to the urban effluent from the area, are similar to reported findings by Chen *et al*., (2005) and Adamo *et al*., (2005). High levels of Zn and Fe in water could also be associated with run offs from the tea farms in the region. Accumulated metal deposition from the time the factory was built can cause immense problems of heavy metals in water in the area surrounding the factory.

The decrease in the concentration of Cu could be associated with reduced geological contribution to Cu enrichment since Cu is normally found to be rich in areas that have low relative disturbances and could therefore, be washed into the surrounding environment. This residual fraction contains naturally occurring minerals which may hold trace metals within their crystalline matrix; extractable copper is mainly associated with oxidizable phase, where it is likely to occur as organically complexed metal species. This behaviour can be attributed to the high affinity of copper to humic substances, which are a fraction of natural organic matter and chemically very active in complexing such metals (Akcay *et al.,* 2003).

In comparison to areas where there are less human activities, the concentration of the metals in most of the studied sites was high. This finding suggests that even though industrial effluents can be deposited in the environment by human activities that spread in the spatial scale within these areas, there are fewer threats from the Pb contamination of water among the sampled sites. The low levels of most metals in water could also be ascribed to dilution and sedimentation in the river. In comparison to WHO (WHO, 1996) guidelines for drinking water, the water of Kapsabet River is therefore, not safe for drinking and other domestic uses. WHO maximum allowable limits for Pb, Zn, Fe and Cu are 0.05 ppm, 5 ppm, 5 ppm and 1.0 ppm, respectively.

4.3.1.2 Spatial variation in metal distribution in soils of Kapsabet River

Results showing the metal concentrations in soils of Kapsabet River during the study period are shown in Figure 4.8. All the four metals investigated displayed significant ($p < 0.05$) differences among the sampling sites. Levels of Pb, Fe and Zn increased along the river profile with highest being sites S3 and S4. However, the concentration of Cu decreased from upstream to downstream. As in the case with water, high levels of Pb, Fe and Zn in sites S3 and S4, which are all located near Kapsabet town, could be attributed to the enrichment of soils with the urban runoffs, use of fertilizers and industrial discharge from Chebut tea industry. The industrial discharge, just like fertilizers and urban runoffs, from the factory may contain traces of metals at low levels, which if continuously deposited on the soils leads to increased concentration of these metals. The addition of fertilizers, chemicals and other substances containing heavy metals to boost agricultural production has often elevated the levels of these metals in the soils, which in

addition to discharge from industrial sources are likely to elevate their levels in the environment (Adamo *et al*., 2002; Berthet *et al.,* 2003; Islam *et al*., 2005; Were *et al*., 2008). The soils of this region are reported to be ultisols which are liable to accumulate metals at higher concentrations than other soils found in Lake Victoria Basin (Mwamburi and Oloo, 1997; Mwamburi, 2003; Ochieng, 2007).
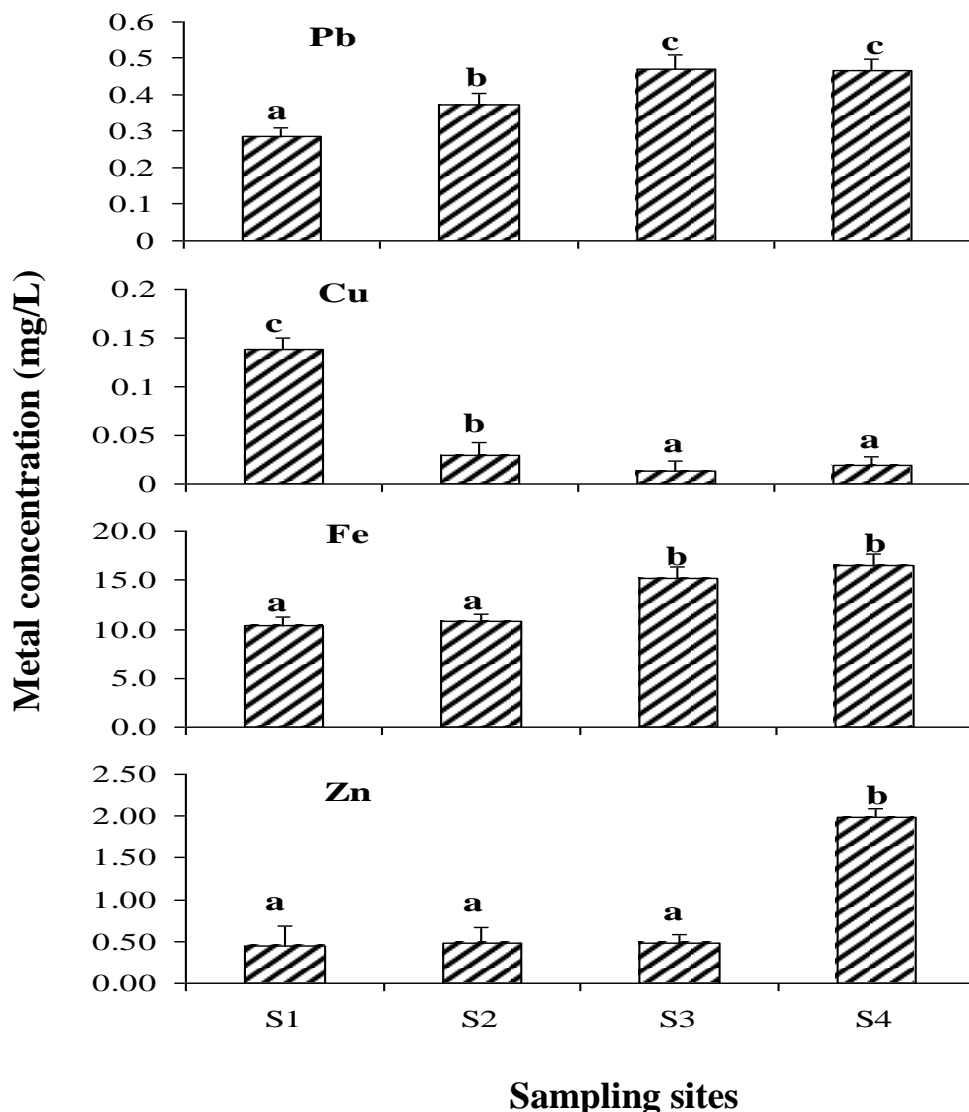
Figure 4.8: Spatial concentration of metals in soils in the four sampling stations during the study period at Kapsabet River (Source: Author, 2012).
Similar lettering a cross each graph represents concentrations that do not differ significantly (p > 0.05) based on t-test.

Levels of heavy metals in soils are indicators of extend of pollution and the use of the agricultural soils within the areas hence to the eventual consumers of products from the soils. A higher threshold value of heavy metals provides evidence of perturbations in the soils due to heavy metals contaminations.

Spatial distribution of heavy metals in the soils showed consistent patterns of variations for all the metals among the four stations. Because of the reactivity of metals with organic compounds (Alloway, 1990), there could be a tendency of the effluents to react with any metal from the geological basins such as Zn. Absence of such organic compounds, could have resulted in increased Zn concentration from the geological sources. Although Kapsabet station reported similarly higher levels of Zn in the river water, this was, however, related to heavy fertilizer uses in the agricultural farms in the close vicinity for tea production rather than from the factory. Thus the presence of metals in a riverine environment may be attributed to numerous non-point sources of pollutants rather than predictable effluents discharged from the industries in close proximity of the river profile. This result is in agreement with similar findings in other aquatic environments (Machiwa, 1992; Mpendazoe *et al*., 1993; Mahimairaja *et al*., 2005; Mbagwu *et al*., 2004; Mandal *et al*., 1998).

4.3.1.3 Spatial variation in metal distribution in sediments of Kapsabet River

Results showing the metal concentrations in sediments of Kapsabet River during the study period are shown in Figure 4.9. Spatial distribution of heavy metals in the sediment

showed consistent patterns of variations for all the metals among the four stations. All the four metals investigated displayed significant ($p < 0.05$) differences among the sampling sites.

Figure 4.9: Spatial concentration of metals in sediments in the four sampling stations during the study period at Kapsabet River (Source: Author, 2012).

Similar lettering a cross each graph represents concentrations that do not differ significantly ($p > 0.05$) based on t-test
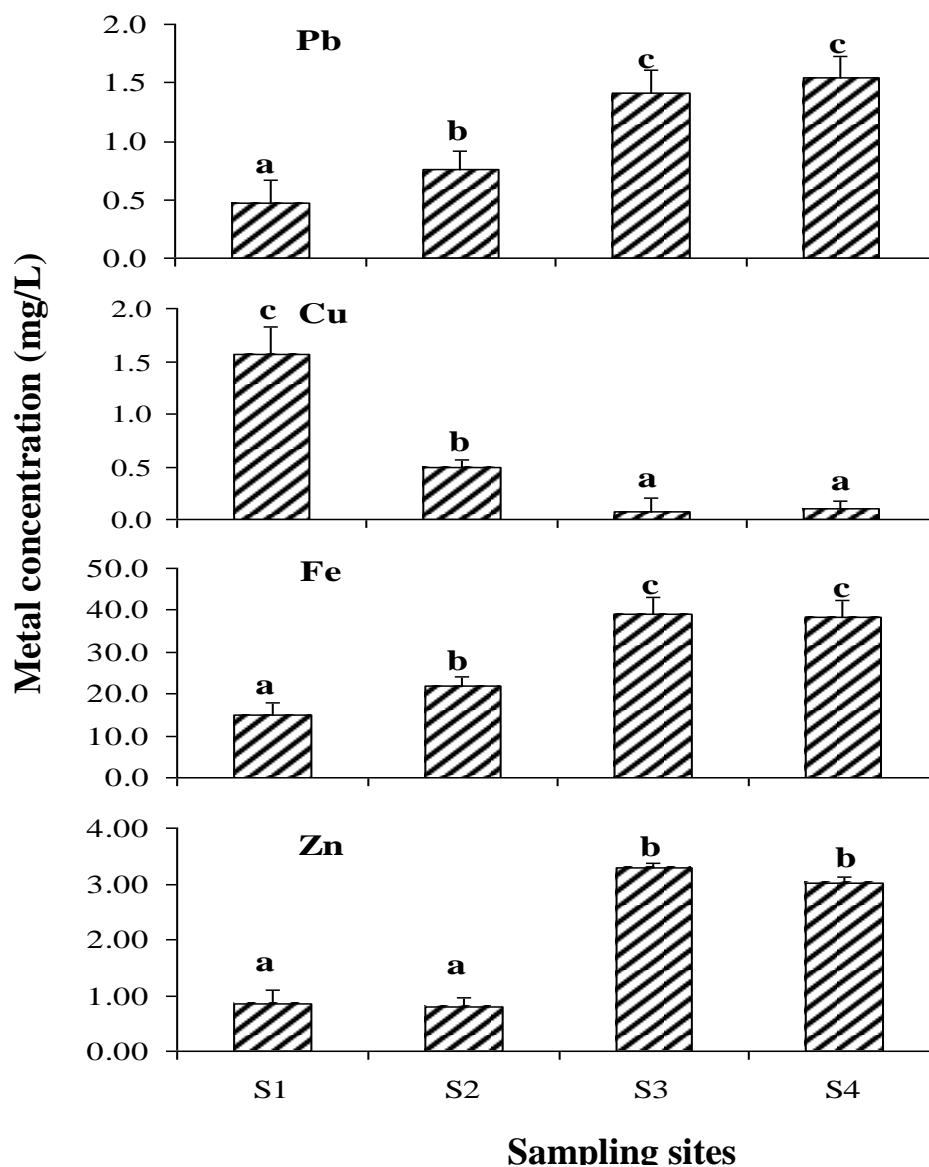
Levels of Pb, Fe and Zn increased along the river profile to be highest in sites S3 and S4. However, the concentration of Cu decreases from upstream to downstream. Most of the metals in the sediments are usually due to differential settling of the metals from water column; therefore, the trends of metals in the sediments reflect the concentration in water and could be explained by the behaviour of metals in water.

However, metal levels were not high enough in comparison to other areas of the world such as Pb levels in sediments (Muniz *et al*., 2004; Muller-Karulis *et al*., 2003 and Fatoki and Mathabatha, 2001). The low levels of Pb could also be ascribed to dilution and depuration in natural waters. Besides the input from natural and anthropogenic sources, Pb distribution in sediments could also be affected by factors such as sediment chemical composition and diagenesis (Salomons and Fŏrstner, 1994). Clark (1998) presented a model that recognized the development of oxidation and reduction horizons, water table fluctuations, and bioturbation as major factors controlling the Pb behaviour within sediments.

4.3.2 Temporal distribution in metal concentration in Kapsabet River

Temporal concentration of metals in the rainy and dry seasons in the study area is shown in Figure 4.10. There was significantly higher metal concentration in rainy season than in the wet season ($p < 0.05$).
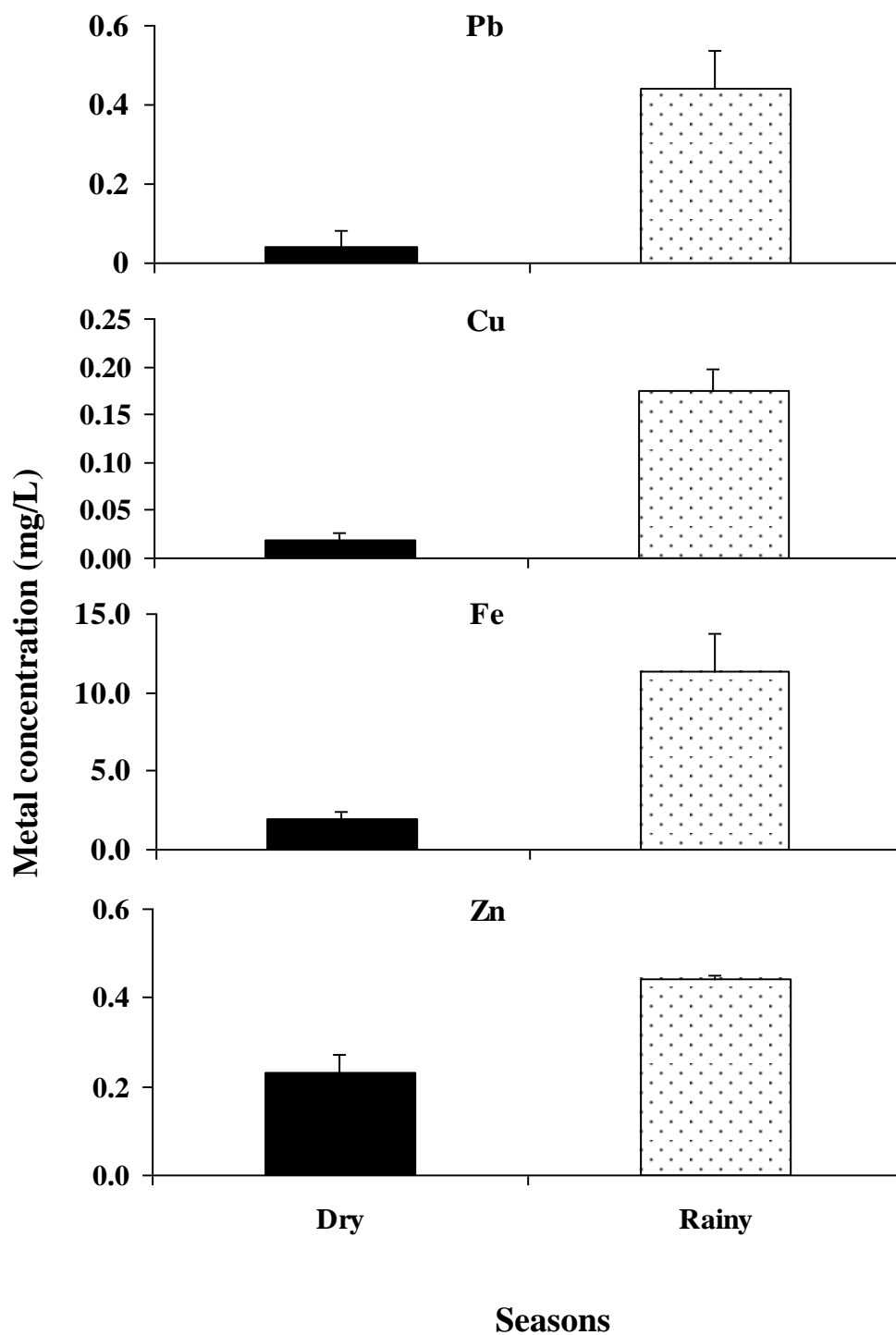
Figure 4.10: Temporal mean (± SD) metal concentration in water in dry and rainy season during the study period in River water (Source: Author, 2012).

The temporal concentrations of metals in soils during wet and dry seasons are shown in Figure 4.11.

Figure 4.11: Temporal mean (± SD) metal concentration in soils in dry and rainy season during the study period in River water (Source: Author, 2012).

 The rainy season had higher concentration of all metals as was found in metal concentration in the sediments between dry and rainy seasons (Figure 4.12). Higher concentration of all the metals in wet seasons could be due to input of metals from external sources into the water body.

Seasons

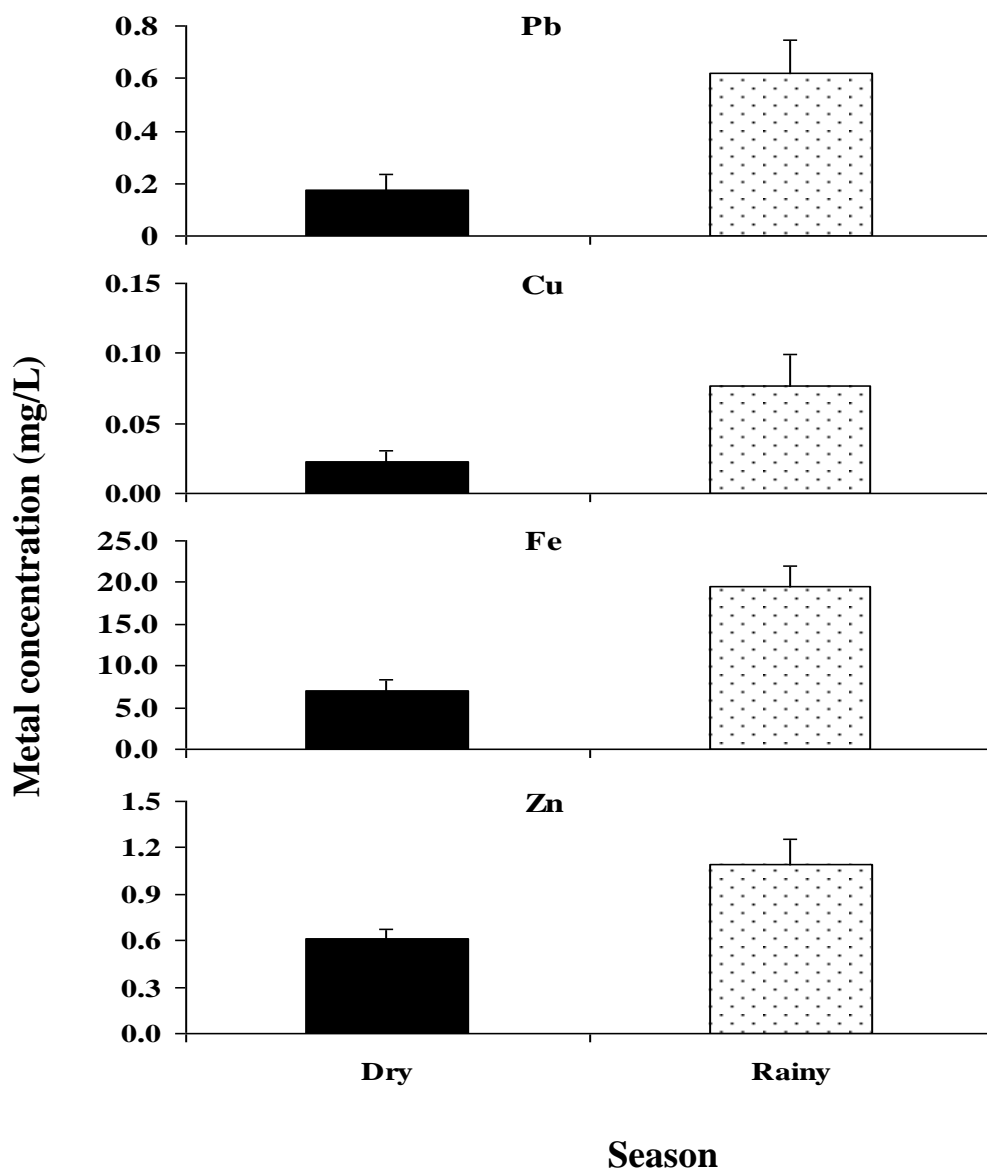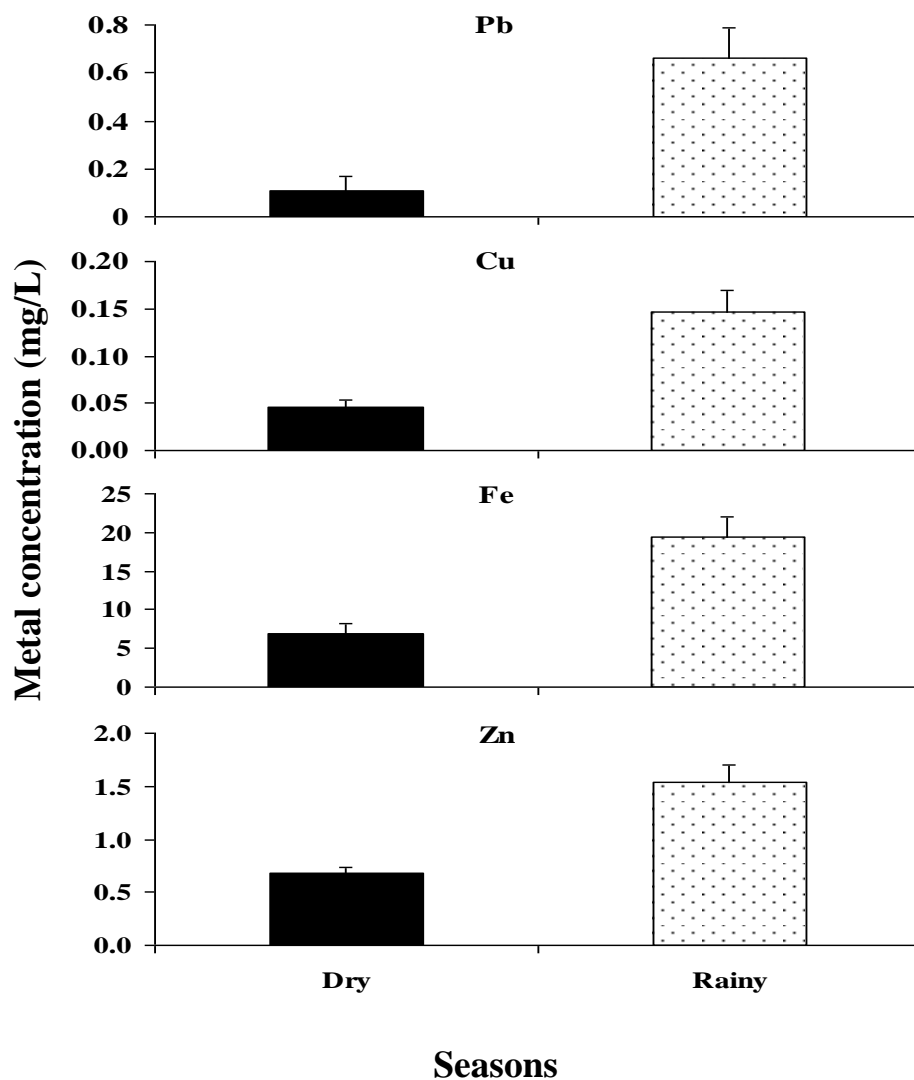**Figure 4.12: Temporal mean (± SD) metal concentration in sediments in dry and rainy season during the study period in River water (Source: Author, 2012)**

4.3.3 Spatial and temporal distribution of the heavy metals in the Kapsabet River

 The spatial and temporal variations of all the metals among the four sampling sites are shown in Table 4.4. There were significant spatial and temporal variations (ANOVA; p <

0.05) in the levels of metals in water soils and sediments with dry season having the highest concentration of all the metals. In the three media, there was a systematic increase in the metal levels along the sites except Cu from site S1 to S4 both in the dry and rainy seasons. This could be attributed to systematic increase in the concentration of metals in water due to increased inputs of external contaminants into the water body from both agricultural and municipal centre. These results also signify that at each site, there is relative contribution of external sources of the studied metals that may not be easily quantified in the surrounding areas because of the non-point nature of the metal pollutants. However, the concentrations of Cu in all the sites within Kapsabet were below the guideline value of European commission for the Drinking Water Directives limit (1998) of Cu of 1 mg/L.

Thus analysis of the metallic concentration indicated that there were significant differences in the levels of Cu among the sampled sites. According to Marjanovic (1990), the low content of free ionic Cu in natural water systems is because Cu forms very stable complexes with humic acids. These acids are abundant in runoffs from farms and some fresh water systems (Marjanovic, 1990; ECSC, 1994). This explains the significantly low levels of Cu in Kapsabet where there is higher density of metal work garages and several workshops as well as motor vehicle and waste metal stalls that contain effluents that are discharged into the nearby waste treatment plants. The wastes then dissociate liberating Cu, which can find their way into the nearby water table and into the drinking water. Seepages of the natural Cu from geological basin can find their way into the water and encourage increased levels of Cu in water.

Table 4.4: Spatial and temporal mean values (± SD, mg/L) of the heavy metals in the four sites in dry and rainy season in water, soils and sediment of Kapsabet River.

	Metal	S1 Rainy	S1 Dry	S2 Rainy	S2 Dry	S3 Rainy	S3 Dry	S4 Rainy	S4 Dry
Water	Pb	0.17 ± 0.01	0.01 ± 0.003	0.23 ± 0.03	0.05 ± 0.005	0.38 ± 0.007	0.09 ± 0.004	0.52 ± 0.01	0.11 ± 0.002
	Cu	0.17 ± 0.04	0.04 ± 0.004	0.14 ± 0.03	0.02 ± 0.006	0.08 ± 0.006	0.02 ± 0.003	0.05 ± 0.01	0.01 ± 0.004
	Fe	1.80 ± 0.16	0.38 ± 0.015	1.15 ± 0.15	0.24 ± 0.05	5.23 ± 0.32	1.73 ± 0.11	8.65 ± 0.42	1.57 ± 0.03
	Zn	0.37 ± 0.03	0.09 ± 0.002	0.33 ± 0.08	0.11 ± 0.008	0.83 ± 0.05	0.29 ± 0.04	0.78 ± 0.06	0.19 ± 0.02
Soil	Pb	0.66 ± 0.05	0.22 ± 0.01	0.67 ± 0.07	0.24 ± 0.07	0.97 ± 0.18	0.13 ± 0.04	0.94 ± 0.05	0.13 ± 0.02
	Cu	0.42 ± 0.04	0.11 ± 0.01	0.12 ± 0.004	0.09 ± 0.003	0.06 ± 0.003	0.01 ± 0.002	0.03 ± 0.006	0.01 ± 0.004
	Fe	13.47±1.86	2.47 ± 0.04	17.75 ± 0.05	5.60 ± 0.76	25.25 ± 0.26	4.47 ± 0.32	34.45 ± 0.23	9.28 ± 0.32
	Zn	1.12 ± 0.07	0.17 ± 0.03	1.10 ± 0.04	0.13 ± 0.13	1.21 ± 0.11	0.16 ± 0.07	5.39 ± 0.11	0.52 ± 0.07
Sediment	Pb	1.25 ± 0.05	0.26 ± 0.03	1.47 ± 0.11	0.38 ± 0.03	3.43 ± 0.13	0.06 ± 0.008	3.75 ± 0.13	0.10 ± 0.06
	Cu	3.05±0.006	0.14 ± 0.02	1.07 ± 0.008	0.17 ± 0.07	0.75 ± 0.006	0.09 ± 0.01	0.61 ± 0.005	0.18 ± 0.06
	Fe	22.43±0.57	2.48 ± 0.28	27.08 ± 0.21	3.69 ± 3.85	64.29 ± 0.42	11.81 ± 0.55	66.95 ± 0.97	12.44 ± 0.33
	Zn	1.97 ± 0.21	0.13 ± 0.003	1.93 ± 0.023	0.23 ± 0.011	7.62 ± 0.09	1.45 ± 0.07	7.64 ± 0.76	1.88 ± 0.06

Tembo *et al*. (2006) established that around Kabwe copper mines in Zambia, where mining of Cu and Zn were the core activities, there were significant differences in the concentration of these two heavy metals within the drinking waters around the town. In sites further away from the mining sites, the Cu concentration rarely exceeded 0.2 mg/l while in sites closer to the mining sites; the Cu concentrations rarely fell below 758 mg/l. In waterlogged soils, aeration of organic matter is lacking and therefore, the humic acid formed in the process of decomposition during long periods of waterlogging, results in increased levels of adsorption of the heavy metals in the sediment, which sinks to the water table and eventually contaminates the water table (Järup, 2003).

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusions

According to the present results obtained from the Kapsabet River, TSS, TDS, BOD, COD and pH exhibited marked variations spatially. The values for the six parameters measured along river all displayed marked spatial variations except temperature among and within the sampled stations. The reported trends are reminiscent of patterns associated with anthropogenic impacts.

There were significant spatial and temporal variations (ANOVA; $p < 0.05$) in the concentration of nitrates and phosphates in water, soils and sediments with the wet season having highest levels in all the media. High concentration of nitrates was attributed to extensive farming which takes place in the vicinity.

There were significant variations of metal concentration in water along the sampling stations, which clearly correlated well with urban effluent discharge along the industrial discharge points in the river. Most of the metals analyzed, except Cu were elevated in water along the urban and industrial discharge points. Significant variations of metals in sediments were also associated with urban and industrial discharge from the factory near the water bodies. The sediments accumulated the metals near sites of industrial discharge than at other sites farther away from the metal discharge sources.

Metal distributions in the soil were linked to discharge of effluents from various anthropogenic sources mainly the industrial sources. There were higher concentrations of metals in soils near the Kapsabet River banks.

Most of the metals that increased downstream the river were generally linked to the factory where there were direct effluent sources. Metal levels generally reduced away from the direct sources of pollutants.

5.2 Recommendations

1. There should be collaboration between the government and communities staying closer to the river on the need to avoid pollution of the adjacent water body, since this will adversely affect the lives of aquatic organisms in the water bodies.

2. Nutrient reduction strategies should be used to control the excessive nutrients load into this river especially during rainy seasons. One such strategy could involve the construction of buffer zones to regulate the inflow of phosphates and nitrates.

3. The effect of long-term stress on organisms, and their ability to adapt to chronic stress due to metal pollutants, is a critical factor in the management of point and non-point source discharges. There is therefore need for the development of laboratory test systems to evaluate chronic stress. Efforts should concentrate on chronic level effects and on bioaccumulation studies.

4. Stricter policy aimed at curbing the disposal of waste associated with heavy metals into the environment be instituted and enforced by the authorities

responsible. Further research could elucidate the most suitable metal reduction strategies and technologies to reduce probabilities of metal poisoning to the Kapsabet River resource users.

5. Soil remediation strategies around the tea factories are called for to reduce the concentration of heavy metals into the water body.

6. Further research is needed to assess the metal forms in the suspended solids, colloidal and hence bioavailability of the metals to the aquatic organisms and humans who will use water from this river, down stream.

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APPENDIX

Appendix I: Quality Standards for Sources of Domestic Water

Parameters	Concentration in ppm except pH
pH	6.5-8.5
NO_3^- -N	10
PO_4^{3-}	0.1
BOD	20
COD	250
TDS	500
TSS	30
Pb	0.05
Cu	1.0
Zn	5.0
Fe	5.0

Source: WHO Geneva, environmental health criteria (1996)