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SPECIATION OF HEAVY METALS IN A TRIBUTARY OF NAIROBI RIVER USING THE JOINT EXPERT SPECIATION SYSTEM (JESS) PROGRAM

By

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DECLARATION

I declare that this thesis is my original work and has not been submitted elsewhere for examination, award of a degree or publication. Where other people's work or my own work has been used, this has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements.

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DEDICATION

This work is dedicated to my family members and all those who assisted me to reach this far.

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ABSTRACT

This study assessed the quality of water in a tributary of the Nairobi River. The study covered six sampling points stretching from Lenana dam to Chiromo Kirichwa Kubwa. Sampling was done twice during the dry and the wet season between July and December 2013. Physicochemical characteristics were analyzed using standard procedures, concentrations of some heavy metals using AAS and speciation analysis using the Joint Expert Speciation System (JESS).The range observed for pH, temperature, DO, COD, BOD, TSS, electrical conductivity, TDS, phosphate, sulphate, chloride, fluoride and nitrite was 6.89-7.77, 18.3 -25.0°C, 8.10-24.29 mg/L, 40-730 mg/L,10.93-25.26 mg/L, 131-414 mg/L, 348-881µS/cm 176-438 mg/L,0.03-5.96 mg/L, 0-68 mg/L, 0.0142-0.886 mg/L, 0.39-2.87 mg/L and 0.002-0.585 mg/L respectively. The range observed for heavy metals was 0.0974-3.1438 mg/L, 0.0092-3.6843 mg/L, <0.01-0.1799 mg/L, <0.005-0.0197 mg/L, <0.05-0.4415 mg/L and <0.02-0.0846 mg/L for Fe, Mn, Cu, Zn, Pb and Cr respectively. Speciation analysis indicated that 69.8% of total iron was in oxidation state III, and the dominant species were free Fe^{2+}ions, sulphates, hydroxides, fluorides, and hydroxide-sulphate complexes. Manganese was observed to be in oxidation state II, and its major chemical forms were Mn^{2+} ions, fluoride and sulphate complexes. Copper was found mostly (>98%) in oxidation state II, and Cu^{2+}ions, sulphate and hydroxide complexes were the major species. Zinc and lead were divalent, and sulphates were their major species. Chromium was trivalent with hydroxide-sulphate and hydroxide complexes being the predominant chemical forms. The results show that the concentrations of Zn, Cu, SO_4^{2-}, Cl^-, NO_2^- and TDS were below the KEBS limits. However, COD, EC, TSS, PO_4^{3-}, F^- Pb, Cr, Fe and Mn were above the KEBS limits for natural water in some sampling points. Cu, Fe and Mn were found to pose health risk since traces of their free ions were obtained in some sampling points. It was generally found that speciation varied with the total concentration of the species and the pH of the system.

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LIST OF ABBREVIATIONS/ACRONYMS AND SYMBOLS

Abbreviation symbol/nomenclature

A………….Absorbance

A_{ij} ....stoichiometric coefficient giving the number of moles of component j in species i

AAS………Atomic Absorption Spectrometry

AES……...Atomic Emission Spectrometry

ASV...........Anodic Stripping Voltametry

ATSDR…..Agency for Toxic Substances and Disease Registry

BDL……….Below detection limit

BOD...…….Biochemical Oxygen Demand

C …………..The concentration of the solution

CE…...…….Capillary Electrophoresis

CICAD…….Concise International Chemical Assessment Document

COD………..Chemical Oxygen Demand

DO………….Dissolved Oxygen

DPASV…....Differential Pulse Anodic Stripping Voltametry

EC……........Electrical Conductivity

Eh………..…Redox potential

EU…........... European Union

FFF…………Free-flow fractionation

GC………….Gas Chromatography

GFAA……...Graphite Furnace Atomic Absorption Spectroscopy

HSDB……….Hazardous Substances Data Bank

IC…………...Ion Chromatography

ICP-MS…......Inductively Coupled Plasma Mass Spectrometry

IPCS…………International Programme on Chemical Safety

IOMC………..The Inter-Organization Programme for the Sound Management of Chemicals

JESS………….Joint Expert Speciation System

KEBS…………Kenya Bureau of Standards

LC……………..…..Liquid Chromatography

M_j……………..Total mass of component j

N_c ……………..Number of components

NAA……………Neutron Activation Analysis

NCWSC……..…Nairobi City Water and Sewerage Company

NEMA…………National Environment Management Authority

NOM………..….Natural Organic Matter

SPADNS……….Sodium-Parasuphophenylazo-1, 8 Dihydroxide-3,6 Naphthalene Disulphonate

TDS…………….Total Dissolved Solids

TSS…………..…Total Suspended Solids

UNEP……..……United Nations Environmental programme

U.S. EPA……..…United States Environmental Protection Agency

WHO……………World Health Organization

β_i……………….Overall equilibrium formation constant for species i

ε ……………….The extinction coefficient

ℓ ………………The distance that light travels through the solution

χ_i ………………Activity of the aqueous species i

γ_i ………………Activity coefficient of species i

λ_{max} ……………The wavelength at which a substance absorbs best

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Water is among the most essential commodities on earth. This is because of its indispensable roles for agricultural and domestic uses; tourism, industrial and cultural purposes and as a medium for numerous physicochemical and biochemical reactions [Oyekunle *et al.*, 2012]. Information obtained from the World Health Organization indicate that about 1.1 billion people representing 17% of the global population lack safe drinking water, majority of who live in China, India, Africa and Middle East [WHO, 2008]. Water pollution problem in the world is increasingly becoming a threat to natural water resources. In developing countries, this situation is attributed to swelling quest of these nations to obtain industrialization status, as well as diversification of national development goals [Kiithia, 2012]. Water pollution makes water harmful to human beings, unfit for industrial use and adversely affects aquatic plants and animals [Budambula and Mwachiro, 2006]. Among the possible pollutants in water, heavy metals have engrossed a lot of attention owing to their high toxicities even at low concentrations. Most heavy metals possess a wide range of oxidation states which determine their physical- chemical forms [Tokalioglu *et al.*, 2000]. Speciation of heavy metals is necessary because different oxidation states of trace metals have been discovered to possess varying degrees of toxicity [Oyekunle *et al.*, 2012].

Nairobi River is the main tributary of the Nairobi River basin which is a complex of several streams flowing eastward through Nairobi City (Figure 1). All of these rivers join east and confluence the Athi River and eventually flow to the Indian Ocean.

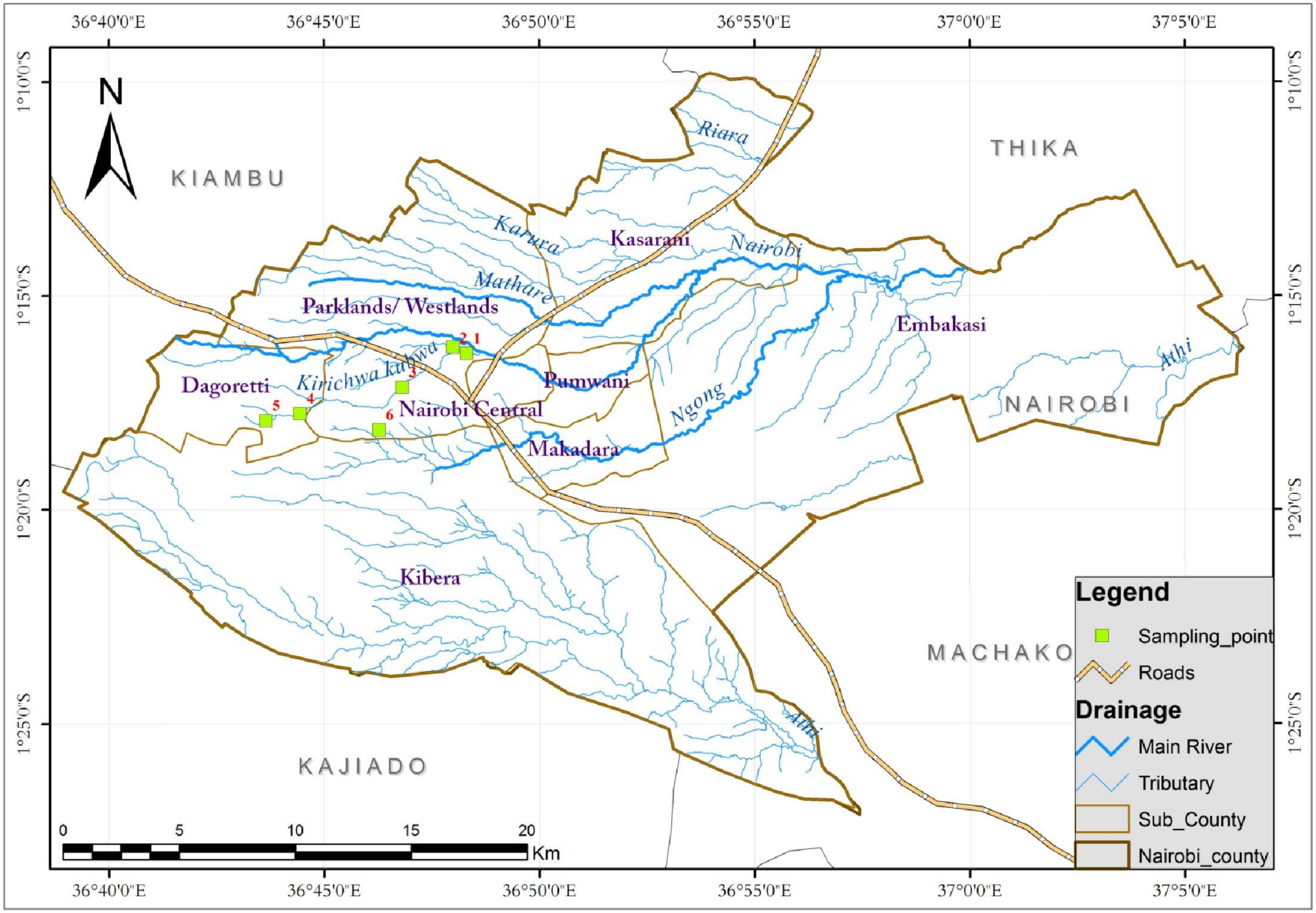

Figure 1: A map of Nairobi including Nairobi River basin. Source: Atonya Stanley, Geology Department University of Nairobi.

The rivers are contaminated with petro-chemicals, garbage, industrial liquid effluents and agro-chemicals among others [Makathimo and Guthiga, 2010]. This situation has led to the blow out of water-borne diseases, loss of supportable livelihoods and biodiversity, decreased availability and access to safe drinking water, as well as the insidious properties of toxic substances together with heavy metal poisoning that affects human productivity [Makathimo and Guthiga, 2010]. While the concentration of heavy metals in the River may have been determined, speciation has not, and yet the chemical risk management of a polluted site by heavy metals depends on the total concentration of heavy metals and also the chemical speciation of the elements. This research focuses on evaluating the present quality of water in a tributary of Nairobi River by monitoring the total concentration of heavy metals and their species.

1.2 Environmental Challenge Facing Nairobi River

1.2.1 Pollution

The most serious problem that is being experienced by the world in the present age is the pollution of the environment mainly by inorganic, organic, and organometallic substances [Mashhood, 2011]. Surface waters are most exposed to pollution mainly because of their easy accessibility for disposal by wastewaters [Wasim *et al.,* 2010]. Both anthropogenic effects like industrial, urban and agricultural activities and natural processes like erosion, precipitation inputs and weathering of crustal constituents degrade surface waters and therefore damaging their use for industrial, drinking, agricultural, or other aims [Wasim *et al.,* 2010]. Nairobi City was established in the early 1900s with a population of about 250,000 [Obudho and Aduwo, 1992]. It was a stop–over point for the then Kenya-Uganda Railway workers [Kiithia, 2012]. At that time, Nairobi boasted of good environmental health, and it was reputed as the green city in the sun. In fact the name Nairobi comes from a Maasai word which means the land of cool waters. This reputation has changed as a result of rapid urbanization and population growth. In 2009, the population of the Nairobi city was about 3.1 million [G.O.K, 2009]. Following the inadequate manner of waste management, residents do not dispose their solid waste properly. As a result, people dump their litter in any other space within the local environment including near the River banks (Figure 2). The consequence is that such rivers are rigorously polluted with man excreta together with other domestic waste. This pollution extends its influences to the international environment, since the waste flows downstream and pollutes bigger rivers at junctions with other tributaries, and the rivers ultimately pour into the Indian Ocean, effectively dispensing the waste across the East African coastline and thus damaging the marine environment [Constance *et al.,* 2011].

Figure 2: Dumpsite located near sampling point 6.

Among the inorganic pollutants of the river water, heavy metals are attracting a lot of attention due to their non-degradable nature and the fact that they frequently accumulate through tropic levels producing a deleterious biological consequence [Kar *et al.,* 2008]. Anthropogenic undertakings such as mining, final disposal of treated as well as untreated waste effluents encompassing toxic metals and metal chelates from different industries like tannery, battery industries, thermal power plants and steel plants, in addition to the indiscriminate use of heavy metal-containing fertilizers and pesticides in agriculture results in worsening of water quality, resulting to serious environmental harm posing danger to human beings [Wasim *et al.,* 2010]. Causes of pollution of the Nairobi River include effluent from car washes and petrol stations, industrial effluent, raw sewage from informal residents as well as raw sewage coming from broken or overloaded sewers [Budambula and Mwachiro, 2006].

1.3 Water Pollution Effects

Human beings are more exposed to pollution presently as compared to other times [Schell *et al.,* 2006]. Some effects of water pollution are recognized immediately while others become visible after several months or years [Ashraf *et al.,* 2010]. Water of poor quality may lead to less drinking water hence dehydration, bad smell, bad living and working conditions, high cost of water supply because it is expensive to treat polluted water, deoxygenation, eutrophication, acid rain and death of aquatic life and human beings. Polluted water is the vehicle for the blow out of water borne diseases such as typhoid, cholera, giardiasis, amoebiasis, diarrhoea among others [Mashhood, 2011]. Studies from the WHO indicate that approximately 1.8 million people are dying every year especially in third world countries as a result of water related diseases [WHO, 2008]. Metal-induced toxicity symptoms range from milder ones such as excessive salivation, nausea, vomiting, diarrhoea with bleeding, abdominal pain, dizziness, headaches, dermatitis, aggressiveness and hallucinations to very serious ones such as lung disease; hepatic damage; liver and kidneys failure; *"itai-itai"* disease; endocrine disruption; mutagenic, carcinogenic and teratogenic effects; circulatory collapse; severe pathological disorder of the central nervous system; reproductive and immune system dysfunction; testicular damage; and pancreatitis [Oyekunle *et al.*, 2012].

1.4 Chemical Speciation of Heavy Metals

Chemical speciation can be defined as the identification and quantification of different chemical forms of elements in any environmental matrix [Fagbote and Olanipekun, 2010]. The main metal species in fresh water includes: simple ionic species and weak complexes, inorganic complexes, differing valency states, lipid soluble complexes, organometallic complexes, metals adsorbed on colloidal particles and particulate metal adsorbed onto or contained within clay particles [Bjornsdottir, 1996]. Knowledge about metal speciation is widely regarded as fundamental to the understanding and forecast of the way metal behaves and its effects on any environmental system [Fytianos, 2001]. This is because it gives information about toxicity, environmental mobility, biogeochemical behavior, bioavailability, and potential risk in general, that are intensely dependent on the chemical species of heavy metals [Campanella, 1996]. Therefore, the problem of metal speciation in waters is of growing interest and significance, and speciation analysis is presently performed regularly by most researchers to control the quality of the environment [Fytianos, 2001].

The main factors influencing the speciation of metals in water have been found to be: the solubility of the metal compounds, the oxidation state of the metals, availability of complexing agents, ion-pair formation, complex formation, adsorption or desorption to particulate material, redox and pH conditions of the environment and biochemical processes[Fergusson, 1990]. Studies on the toxicity of heavy metals show that the free hydrated ion is the most toxic form. This is because the free metal ion is significantly easier and faster adsorbed on suspended particles [Odobasic, 2012]. If the ions are bound to Natural Organic Matter (NOM) or adsorbed to solids, they are no longer free and therefore less bioavailable [Sjostedt, 2012].

There are many different speciation techniques available, which use different principles for separating the different forms of the metals. There are direct measurements of the free ion, for example, by potentiometry and ion-selective electrodes, but these methods are selective and usually require high concentrations of the metal. There are methods which separates compounds by size since the smaller fractions include the more potentially toxic free ions and dissolved inorganic complexes. These methods include various forms of ultra-filtration, dialysis, size-exclusion chromatography and field-flow fractionation (FFF) [Sjostedt, 2012].

Over the past decade, numerous advances in material science have resulted into the development of a wide extent of analytical tools for chemical speciation. Computer based models for solution speciation have been developed, for example MINTEQA2 [Allison *et al.*, 1990], WATEQ4F [Ball and Nordstrom, 1991], ECOSAT [Keizer, 1991], PHREEQC [Parkhurst, 1995] JESS [May and Murray, 2008] among others. These computer centered models are grounded upon equilibrium constants and/or Gibbs free energy values so as to determine metal speciation from the solution chemistry (temperature, concentration, pH, redox potential, organic complexes, and adsorption/desorption cites). Both methods rely on mass balance, as well as equilibrium conditions. JESS program has been subjected to some level of development within the recent years because reliable thermodynamic data has turned out to be available and can offer some predictive estimates of metal behaviors. JESS contains a great deal of coded knowledge about chemical speciation, and about the way chemical speciation calculations should be performed. Its knowledge takes the form of explicit rules, fuzzy logic and even Bayesian-type functions. These decision making techniques assist in tasks that require considerable expertise, which otherwise can prove difficult to accomplish without an error [May and Murray, 2008].

In JESS modeling, speciation is calculated by using thermodynamic parameters for the appropriate reactions within aqueous media. All types of chemical equilibria, including protonation, redox solubility, complex formation and adsorption can be modeled. Variation in relative amounts of components, ionic strength and temperature is taken into account. The profile of all species is obtained regardless of how little of each one may be present. The models are at their most powerful when predicting the chemical behavior of complex mixtures [May and Murray, 2008].

JESS has a system in which all thermodynamic values are assessed during database compilation and assigned a weight. These weights indicate the best assessment of the reliability of each value. Every constant considered worthless is given zero weight and thus has no influence on subsequent calculations. Apart from specifying some basic information about the chemical system one may wish to model, one does not concern himself/herself with the means by which the computer makes a decision because JESS provides this input by default. In this way, one rapidly accomplishes an initial calculation and successfully obtains speciation distribution. The thermodynamic parameters in a JESS database span a variety of conditions, including values for different solvents, background electrolytes, ionic strengths and temperatures. This is unlike other computer models for performing equilibrium calculations that reduce all the available data to a single value at a particular reference state. Therefore, JESS can employ values directly that happens to be measured under the condition of the model. Where these exact conditions are missing, JESS can use values under conditions as close as possible. Errors arising from imperfect methods of corrections such as Debye-Huckel functions are thus minimized [May and Murray, 2008].

1.5 Problem Statement

Much concern has been raised due to the presence of heavy metals in the environment because they are toxic, and are a threat to human and marine life at elevated concentrations; they also lead to environmental degradation [Kar *et al*., 2008]. Heavy metals in water exist in different oxidation states and different chemical forms so their toxicity changes depending on the form in which they are found. Consequently, the knowledge of total concentration of metals in contaminated water is not sufficient for proper information regarding their harmful effect. Mobility, toxicity, bioaccumulation and biodegradability depend on specific physicochemical form in which a metal is found [Odobasic, 2012].

Nairobi City has experienced rapid industrialization and increase in population during the last century [Budambula and Mwachiro, 2006]. Infrastructure that deals with waste disposal has not been developed to match with this rapid growth in population. Therefore, problems have arisen with regard to garbage, industrial and human waste disposal leading to water pollution. Heavy Metals enter the aquatic ecosystem mainly through the disposal of chemical and metal wastes from industrial, mining and agricultural undertakings. Heavy metals accumulate in the tissues and organs of living aquatic organisms thereby affecting the normal processes of the body. This water is used for crop irrigation on the river banks and also for domestic purposes thus threatening human health. Previous reports on Nairobi River give the total concentrations but not speciation of the heavy metals for example by Ohayo [1996], Budambula and Mwachiro [2006] and Masese [2010]. It is known that the total concentration of heavy metals gives little information about toxicity, environmental mobility and potential risks in general which are strongly dependent on chemical species of heavy metals. This project aims at determining speciation of some metal ions in a tributary of Nairobi River. It is envisaged this would fill the gaps presented in previous studies. It will also fill the information gaps on some areas that had not been sampled before.

1.6 Objectives

1.6.1 Overall Objective

To investigate the current quality of water in a tributary of Nairobi River by assessing the level of physicochemical parameters, anions and some heavy metals including their speciation.

1.6.2 Specific Objectives

1.To determine the temperature, pH, electrical conductivity, TDS, DO TSS, BOD, COD and the concentration of NO_2^-, Cl^-, F^-, PO_4^{3-} and SO_4^{2-} from the selected sampling points.

2. To determine the level of Cu, Pb, Mn, Cr, Fe, and Zn from the selected sampling points.

3. To assess the seasonal variation of heavy metal ion concentration and other physicochemical parameters from the selected sampling points.

4. To determine speciation of Cu, Pb, Mn, Cr, Fe, Zn, NO_2^-, Cl^-, F^-, and SO_4^{2-} from the selected sampling points.

1.7 Justification

Nairobi River and its tributaries flow through the residential and industrial areas of Nairobi. It receives and drains untreated and treated discharges of various types. Water from this river is used for agriculture and domestic purposes especially by people living downstream. It has been reported that the river water contains heavy metals [Budambula and Mwachiro, 2006]. The concentrations of these heavy metals accumulate and increase in the bodies of animals and different parts of plants through biomagnifications. Exposure to heavy metals may lead to kidney damage, developmental retardation, various cancers and even death. Knowledge of chemical speciation of heavy metals gives more information on toxicity, bioavailability, mobility and potential risks of heavy metals. Speciation of heavy metals is therefore crucial to the understanding and prediction of metal behaviors and its impacts on any environmental system. Information about speciation of heavy metals in Nairobi River, is conspicuously lacking thus this research will provide more information on the quality of water from the river.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy Metals in Water

Heavy metals refer to elements which have atomic weights of between 63.546 and 200.590 and specific gravity greater than 4.0 [Bala *et al*., 2008]. Metal and metalloids can be classified into three groups, based on their toxicity [Fernandez *et al*., 1992]. The metal/ metalloids contained in the first group are toxic in the entire concentration range and do not have known biological functions; this group includes lead, mercury and cadmium. The metals of the second group (which comprises of arsenic, bismuth, indium, antimony, and thallium) also contains no recognized biological purposes, but are less toxic; though, they are still toxic if present in more than trace concentrations. The last group includes essential metal/metalloids such as zinc, copper, cobalt, iron and selenium which are necessary for numerous biochemical and physiological procedures, and are toxic beyond certain concentrations [Adrian, 1995]. All heavy metals present in surface waters exist in the form of dissolved phases, colloids and particulates, although the concentrations of dissolved phases are normally low [Kennish, 1992] compared to their levels in the underlying associated sediments [Oyekunle *et al*., 2013]. The metals behavior in ordinary waters is set up as a function of the suspended sediment constituents, the substrate sediment constituents, and the water chemistry. The chemistry of water system regulates the proportion of adsorption and desorption of metals into and from the sediment [Connel *et al.*, 1984]. Adsorption removes the metals from water column and stores the metal in the substrate while desorption returns the metals to the water column where recirculation and bioassimilations may occur. Metals could be desorbed from the sediment in case the water experiences the following:

Redox potential decrease: This often occurs under oxygen-deficient conditions and usually changes the composition of metal complexes and discharges the metal ions into the overlying water.

Decrease in pH: A lower pH may lead to increased competition between hydrogen and metal ions for binding sites. It may also dissolve metal carbonate complexes releasing free metal ions into the water column.

Increase in salinity: High salt concentrations increase the competition between cations as well as metals for binding sites. Frequently metals would be drawn into the underlying water [Connel *et al.,* 1984].

Metal solubility is principally controlled by environmental pH, its various types of species and oxidation states, the organic ligands and the redox environment of the aquatic system [Grosbois *et al*., 2006 and Ochieng *et al*., 2009]. Clark *et al.,* [1998] justified that the redox potential of the sediment can have an effect on metal trapping directly through change in oxidation state of the metal itself or indirectly through a change in the oxidation of the ions that can form complexes with the metal.

2.2 Properties and Sources of Selected Heavy Metals

Heavy metals enter into the environment by natural and anthropogenic means. Such sources may include:

- Non-point sources- this involves input of pollutants by atmospheric transport (e.g. soil erosion, urban runoff, sewage effluents, industrial discharge, pest or disease control agents applied to plants, among others).
- Point sources – this is where pollutants are introduced by rivers and streams.

- A natural change in the mineralogy of the sediments with a relative decrease or increase in the trace metals [Greaney, 2005].

After entering the aquatic environment, trace metals are distributed among waters, biotic and sediment compartments [Greaney, 2005]. Some individuals are primarily exposed to heavy metals in the work place. However, the main exposure for most people is through diet (water and food) [Morais *et al.*, 2012].

2.2.1 Chromium

Chromium is a metallic element which belongs to group VI of the periodic table. It occurs predominantly in its Cr (III) and Cr (VI) oxidation states. Chromium occurs naturally in soil, rocks, animals, plants and in volcanic dust and gases [Dernbach, 2008]. It is reported that the average chromium concentration in rain water ranges from 0.2µg/L to 1.0µg/L [Kieber and Heiz, 1992]. According to the WHO, the total chromium concentration in drinking water is usually less than 2µg/L although concentrations as high as 120µg/L have been reported [WHO, 2003]. The primary users of chromium are the metallurgical, refractory and chemical industries. In metallurgical industries, chromium is used to produce stainless steels, cast irons and non-ferrous alloys. In the chemical industry, chromium is used mainly in numerous commercial processes including leather tanning, electroplating, pulp production, milling, mining, and wood preservation [Cornelis *et al.*, 2005]. The presence, concentration and form of chromium in discharged effluents depend mainly on the chromium compounds utilized in the industrial process, the pH and the presence of other inorganic and organic processing wastes [Rakhunde *et al.*, 2012].

2.2.2 Lead

Lead is a metallic element which belongs to group IV A of the periodic table. Its properties include: high density, low melting point, malleable, low strength, ductile, acid resistance, and chemical stability in water, air and earth [UNEP, 2010]. There are three chemical forms of lead namely: inorganic lead compounds, metallic lead and organic lead compounds. The three oxidation states of lead are Pb (0) which is the elemental form, Pb (II) and Pb (IV). It makes up only about 0.0013% of the earth's crust meaning that it is not an abundant element [UNEP, 2010]. Pb forms the least stable and most reactive organometallic derivatives compared to other group IV metals in the periodic table [U.S. EPA, 2005b].

The important sources of lead into the environment can be grouped into the following categories:

- Natural sources─ this involve releases which result from mobilization of lead which occurs naturally in the earth's crust and mantle such as weathering of rocks and volcanic activity.
- Anthropogenic discharges which result from the mobilization of Pb impurities in raw materials, for example fossil fuels and other extracted, recycled and treated minerals.
- Anthropogenic releases which result from Pb used intentionally in products and processes due to release by manufacturing, use, disposal or incineration of products. [UNEP, 2010].

Lead exposure occurs as a result of ingestion of food stuffs, water and from the air. Ingestion of dust ,contaminated soil and old lead-based paint due to hand to mouth activities may be important regarding to lead intake by young children. Lead intake via drinking water can be a more dominant source when tap water systems with leaded pipes are used [WHO/UNECE, 2007].

The daily intake of Pb varies by country and the sources vary with the diet. In the European Union, vegetables, fruits, cereals, beverages and bakery wares are the main sources of dietary lead [EU SCOOP, 2004]. Some recent studies show that lead paints are still being used in some countries in Africa [Mathee *et al.*, 2007]. Airborne Pb may contribute significantly to exposure, depending on the factors such as occupation, proximity to busy roads, use of tobacco, lead smelters and repair workshops [IPCS, 1995]. In nations where leaded petrol is still used, the major lead exposure pathway is inhalation of vehicle emissions particularly close to high traffic roads [UNEP, 2010].

2.2.3 Copper

Copper is a transition metal that is stable in its metallic state and forms divalent and monovalent cations. Metallic copper is a good thermal and electrical conductor, ductile and malleable [WHO, 2004]. Copper is used to make pipes, electrical wiring, coins, building materials and cooking utensils. Copper compounds are used as fungicides, algaecides, insecticides and wood preservatives, and in manufacture of azodye, electroplating, lithography, and petroleum refining [WHO, 2004]. Copper compounds are normally added to animal feeds and fertilizers as a nutrient to support animal and plant growth [ATSDR, 2002].

The sources of copper in the atmosphere include wind dispersion of particulate geological materials and particulate matter that result from smokestack emissions [WHO, 2004]. These sources collectively account for only 0.4% of copper released into the environment [Barceloux, 1999]. Studies from Canada, Europe, and USA indicate that copper levels in drinking water can range from ≤ 0.005 to >30 mg/L, with the main source most often being the corrosion of interior plumbing [U.S. EPA, 1991]. Water and food contribute much to copper exposure in developed countries. In general, copper intakes for adults range from 1 to 3 mg/day [IOMC, 2001]. Use of mineral supplement will increase exposure by about 2 mg/day. According to the World Health Organization, drinking water contributes to 0-1 mg/day in most situations. Thus daily copper intakes for adults range from 1 to 5 mg/day [WHO, 2004].

2.2.4 Manganese

Manganese occurs naturally in the environment, and is found in rocks, water, soil and food. It exists in eleven oxidation states which range from -3 to +7; however the most common ones are +7, +4 and +2. It is ubiquitous in the environment and makes up about 0.1% of the earth's crust [CICAD, 2004]. Manganese compounds have a variety of uses; for example, manganese chloride acts as a catalyst in the chlorination of organic compounds; it is used in animal feed to supplement essential trace minerals and in dry-cell batteries. Manganese sulphate is used primarily as a livestock supplement, as a fertilizer; it is also used in some fungicides, glazes, varnishes, and ceramics. Potassium permanganate is used as a disinfectant, as an oxidizing agent and anti-algal agent; for tanning, metal cleaning, and bleaching; as a purifier in water and waste treatment plants and preservative for fresh flowers and fruits [HSDB, 1998].

Important natural sources of manganese include sediments, soils and rocks [Reimer, 1999]. Crustal rocks, ocean sprays, forest fires, vegetation and volcanic activity are the primary natural sources of manganese in the atmosphere. The anthropogenic sources of manganese include municipal waste water discharges, sewage sludge, mining and mineral processing, emissions from alloys, steel, and iron production, combustion of fossil fuels and fuel additives [CICAD, 2004].

2.2.5 Zinc

Zinc is a lustrous bluish- white metal that is found in group II B of the periodic table. It is crystalline and brittle at ordinary temperatures. Zinc occurs naturally in water air and soil, but its concentrations are rising unnaturally due to the addition of zinc through human activities. It is used principally for galvanizing iron, for gutters and roofing in building and construction, and for negative plates in some electric batteries. In the rubber industry, zinc oxide is used as an activator and as a white pigment in paints in the automobile industry. As a pigment, zinc is used in cosmetics, plastics, photocopier paper, wallpaper and printing inks [Greaney, 2005]. Drinking water contains certain amount of zinc whose concentration may be higher when it is stored in metal tanks. Zinc is mostly added during industrial activities like steel and coal processing, mining and waste combustion [Greaney, 2005].

2.2.6 Iron

Iron is the second most profuse metal within the earth's crust, and it accounts for about 5% [WHO, 2003]. Elemental iron is not often found in nature since the iron ions freely combine with oxygen and sulfur-containing compounds to form hydroxides, oxides, sulfides and carbonates. Iron is used as constructional material, among other uses for drinking water pipes. Iron oxides are used as pigments in plastics and paints. The mean concentration of iron in river waters has been reported to be approximately 0.7 mg/L. According to the WHO, the concentration of iron in drinking water is normally less than 0.3 mg/L but may be higher in countries that use various iron salts as coagulating agents in water treatment plants and where galvanized iron, steel and cast iron are used in pipes for distributing water. Food is the major source of iron exposure to human beings; however, drinking water containing 0.3 mg/L would contribute approximately 0.6 mg to daily intake [WHO, 2003].

2.3 Roles of Heavy Metals in Human Health and Toxicity

Environmental pollution by heavy metals has led to numerous adverse influences on human health [Okoro *et al*., 2012]. Heavy metals are problematic due to their non-degradability and persistence in the environment [Yuan *et al*., 2004]. They are also harmful because they tend to bioaccumulate. Bioaccumulation implies a greater amount of a chemical in a biological organism with time, compared to the amount of chemical in the environment. Interests in metals like copper, zinc, manganese and iron that are essential for metabolic functions in organisms rely on their nutritional value as well as their toxicity. Metals such as lead and chromium may exhibit extreme toxicity even at low concentrations under certain conditions [Okoro *et al.,* 2012].

2.3.1 Chromium

Cr exists in the environment mainly in two oxidation states, Cr (VI) and Cr (III). Cr (VI) is a powerful oxidizing agent and is 10 to 100 time's toxic than Cr (III) [Singh and Kalamdhad, 2013]. Cr (III) is the most stable in nature and biological systems. It is also not found to be carcinogenic to humans [Rakhunde *et al*., 2012]. Cr (III) is an essential trace element inside the body and it integrates with numerous enzymes in transforming proteins, sugar and fat. Due to their solubility and acidic nature, soluble Cr (III) substances can be irritating to the eyes and skin [Rakhunde *et al*., 2012]. Cr (VI) has been found to cause cancer to human beings [Rakhunde *et al*., 2012]. Other health effects attributed to Cr (VI) are skin rash, nosebleeds, ulcers, respiratory problems, kidney and liver damage, weakened immune systems, alteration of genetic material and death [Rakhunde *et al*., 2012]. According to the WHO the maximum limit of Cr in water stipulated for drinking or domestic purposes is 0.05 mg/L [WHO, 2011].

2.3.2 Lead

Lead plays no role in human body; its exposure can lead to many biological effects which depend on its level and duration [UNEP, 2010]. Impaired neurodevelopment among children is one of the greatest critical influences and could arise from exposure in the uterus and during early childhood [WHO/UNECE, 2007]. Lead exposure to children is linked to a lower intelligence quotient (IQ), learning disabilities and behavioral effects. Reports indicate that lead is damaging even at blood lead concentrations below 0.01mg/L and there could be no threshold implying that it is not possible to form a “safe” level of Pb in the blood of fetuses and children [Canfield *et al.,* 2003]. The doubling of blood lead rate from 10 to 20µg/dl has been associated with an average loss of 1 to 3 points of IQ [Winneke and Kraemer, 1997]. Enormously high blood lead in children (above 70µg/dl) could result into severe neurological impact leading to convulsions, lethargy, coma and death [UNEP, 2010]. Long term exposure to lead at work place has been realized to drop performance within certain tests of nervous system function, thus resulting in weakness in wrists, fingers, and ankles [US ATSDR, 2005].

A high blood lead level (above 40µg/dl for a period of years) is known to reduce fertility especially among men and raise the risks of spontaneous abortion, preterm delivery and reduced fetal growth for offspring. Maternal blood lead proportions of approximately 0.01 mg/L have been attributed to amplified risks of hypertension during pregnancy, impulsive abortion as well as impaired neurobehavioral formation on the offspring [Belinger, 2005]. Although there is no proof that Pb can cause cancer in humans, a number of studies have proposed an association between lung cancer and lead exposure [Steenland and Boffetta, 2000 and Lustberg and Silbergeld, 2002]. Lead is hypothesized to be a co-carcinogen permitting or growing the genotoxic influences of other agents [Silbergeld, 2003].

2.3.3 Copper

Copper is a fundamental micro-nutrient which is required by most organisms for normal metabolic functions. In human bodies, copper helps to produce the haemoglobin [Greaney, 2005]. Studies show that lower doses of copper can cause symptoms typical of food poisoning such as headache, nausea, vomiting and diarrhoea [Stenhammar, 1999]. Long-term daily intakes of copper below recommended requirement can lead to neutropenia, anaemia, and bone demineralization in malnourished children [IOMC, 2001]**.** Copper becomes toxic when an organism is unable to regulate excessive concentrations. The free Cu^+ is the most toxic form with toxicity decreasing in the order $Cu^+ > Cu^{2+} >$ inorganic copper> organic copper [Jones and Bolam, 2007]. Individuals ingesting high doses of copper present with gastrointestinal bleeding, haematuria, intravascular haemolysis, methaemoglobinaemia, acute renal failure, hepatocellular toxicity, and oliguria [Agarwal *et al.,* 1993].

2.3.4 Manganese

Manganese is one of the most essential trace elements, but it is also toxic at high concentrations. It participates in hemopoietic functions and the transformation of genetic information. Manganese is also useful to the synthetic process of thiamine and ascorbic acid; its deficiency in persons is connected to delayed blood coagulation as well as hypercholesterolemia and abnormal manganese metabolism can contribute to diabetes mellitus [Noroozifar *et al*., 2007]. Problems resulting from a high concentration of manganese are manganese pneumonitis (fever, cough, and malaise), liver damage, neurotoxicity, chronic respiratory tract inflammation, stillbirth, and birth defects (like cleft lip, heart defects, imperforated anus and deafness) [Etzel, 2003]. The present World Health Organization standard for maximum manganese levels in drinking water is 0.4 mg/L for human health [Noroozifar *et al*., 2007].

2.3.5 Zinc

Zinc is one of the trace elements considered to be essential for human health. Reports show that some parts of the body contain zinc with the highest concentrations being found in the urethra and prostate [ATSDR, 1994]. The allowable limit for zinc in drinking water is 5.0 mg/L. It can cause a bitter astringent taste and turbidity in alkaline waters at concentrations above 5.0 mg/L [Okoro *et al*., 2012]. Symptoms due to excessive zinc consumption include; dizziness, gastric ulcers, nausea, lethargy, muscle pain, impairment of immune function, vomiting, headaches, dehydration, stomachaches, poor muscle coordination, fatigue and possible renal failure [ATSDR, 1994].

2.3.6 Iron

Iron is an essential nutrient in human nutrition. However, it can be damaging when it is excess in the body. Approximations of the minimum daily requisite for iron depends on sex, age, iron bioavailability, physiological status, and spread from about 10 to 50 mg/day [WHO, 2003]. The roles of iron in the body are transportation of oxygen to the cells from the lungs, catalase production, sense of direction and production of energy [Lieu *et al.,* 2001]. Excess iron damages the body by replacing other vital minerals such as copper, zinc and manganese thus causing enzyme dysfunction, inflammation and stimulating the growth of common bacteria leading to chronic infection [Lieu *et al.,* 2001]. The physical ailments associated with iron poisoning include; diabetes, cancer, nervous system diseases (such as Alzheimer’s disease, Parkinson’s disease, and behavioral abnormalities comprising violence and autistic characteristics), kidney problems, arthritis and multiple scleroses. It may also comprise milder minor forms of inflammation like random pains and aches, premenstrual syndrome and headache syndromes [Lieu *et al.,* 2001].

2.4 Speciation of Heavy Metals in Water

2.4.1 Chromium

The most common forms of chromium in natural water are Cr (VI) mainly present as the chromate ion, CrO_4^{2-} and Cr (III) principally as an aqua-ion [Comber and Gardner, 2003]. The distribution of compounds containing Cr (III) and Cr (VI) depends on the pH, redox potential, kinetics of the redox reactions, presence of oxidizing or reducing compounds, formation of Cr (III) complexes or insoluble Cr(III) salts and total chromium concentration [Rakhunde *et al.,* 2012]. According to the WHO, Cr (VI) salts are more soluble than those of Cr (III), this makes Cr (VI) relatively mobile [WHO, 2003]. Cr (III) species are predominant chromium forms in surface waters at lower pH (5-7) and in the presence of readily reducible organic substances [Swietlik, 1998]. The behavior and nature of various chromium forms found in natural waters is different from those present in waste water because of altered physical-chemical conditions of effluents originating from various industrial sources [Rakhunde *et al.,* 2012].

According to thermodynamic calculations, inorganic Cr (III) ions in aqueous solution exist as hydroxo species including Cr^{1+}, $Cr(OH)^{2+}$, $Cr(OH)_4^-$, $Cr(OH)_3$, $Cr_2(OH)_2^{4+}$,and $Cr_3(OH)_4^{5+}$ and a mixed ligand complex as $Cr(SO_4)^+$ and $Cr(OH)Cl^+$. $Cr (OH)^{2+}$ is dominant at pH 5 whereas $Cr(OH)_3$ prevails at pH 8 [Swietlik, 1998]. Free aqua cations, chloro, polynuclear cationic species together with sulphate complexes are ignored because they don't contribute much to surface waters under typical pH conditions [Rakhunde *et al.,* 2012]. Cr (VI) may be present in aqueous solutions mainly as dichromate, chromate, hydrogen chromate, hydrogen dichromate, and chromic acid. $HCrO_4^-$ and CrO_4^{2-} can be found in typical surface waters when the concentration of chromium is less than 5µg/L. The chromate ion predominates at $pH>7$ whereas hydrogen chromate is predominant at $pH<6$ [Sperling *et al.,* 1992]. Figure 3 shows species distribution of Cr (III) and Cr (VI) in aqueous system.

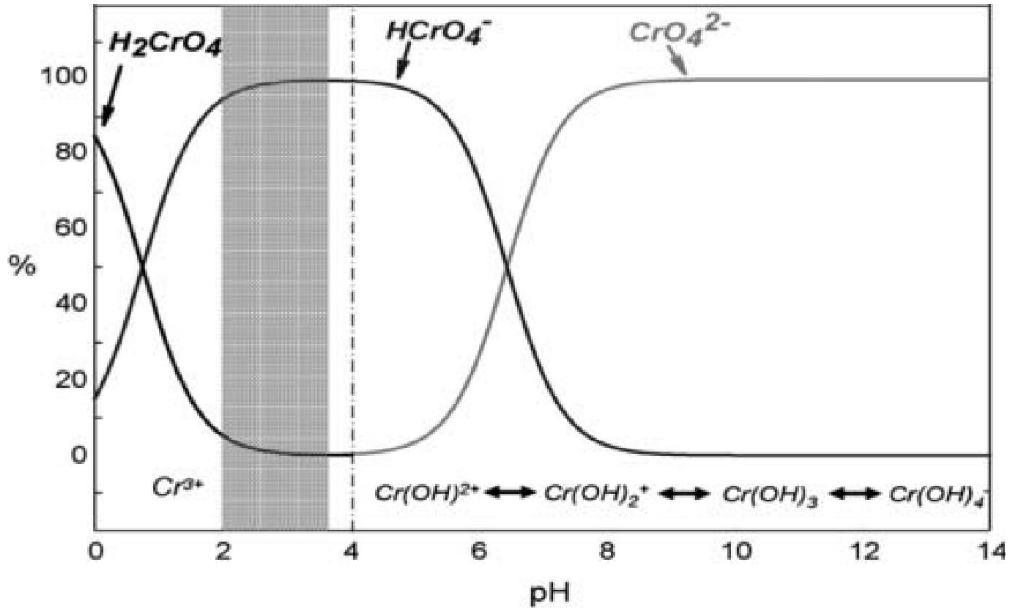

Figure 3: Species distribution of Cr (VI) and Cr (III) in aqueous system [Hagendofer and Goessler, 2008].

2.4.2 Lead

In the aquatic environment, lead may occur as organic complexes with dissolved humus material (binding is rather strong and limits availability) or ionic form (highly mobile and bio-available) or close to colloidal particles (strongly held and less mobile in such a form than as free ions) or attached to solid elements of clay or dead residues of organisms (very narrow mobility and availability) [UNEP, 2010]. The speciation of lead in aquatic environment is controlled by factors such as pH, sorption, salinity and biotransformation processes. Lead is present in acidic aquatic environment as ionic lead, $PbSO_4$, $PbCl_4$, ordinary hydroxide $Pb(OH)_2$ and cationic forms of lead hydroxide [UNEP, 2010].

In case of fresh water, lead could partially occur as divalent cation (Pb (II)) at pH below 7.5, but in complexes with dissolved carbonate, it forms insoluble $PbCO_3$ under alkaline conditions. Lead –organic matter complexes are stable to pH 3, with the affinity growing with rise in pH but declining with increased water hardness [U.S. ATSDR, 2005]. In cases of alkaline waters, species of lead comprises of $PbCO_3$ and $Pb(OH)_2$. In case of fresh water, lead typically creates solid complexes with CO_3^{2-} and OH^- as well as weak complexes with Cl^- [UNEP, 2010]. The main form of lead contained in fresh water at low pH (≤ 6.5) is largely Pb^{2+} ions and less abundant inorganic complexes include $Pb(SO_4)_2^{2-}$, $Pb(HCO_3)$, $PbCl_2$, $Pb_2(OH)_2CO_3$ and $PbCO_3$. At higher pH (≥7.5), lead creates hydroxide complexes like ($Pb(OH)_2$, $[PbOH]^+$, $[Pb(OH)_3]^-$ and $[Pb(OH)_4]^{2-}$). Speciation of lead in sea water is controlled by chloride concentration and the prime species are $[Pb(OH)]^+ < [PbCl]^+ < PbCl_2 < PbCO_3 < [PbCl_3]^-$ [Fernando, 1995]. Figure 4 below shows speciation diagram for Pb^{2+}+H^+, Cl^-, SO_4^{2-}, HPO_4^{2-} and CO_2 in fresh water with the following total concentrations $[Cl]_T$=0.23mm/dm^3, $[SO_4^{2-}]_T$ = 0.42mm/dm^3,$[HPO_4^{2-}]_T$ = 0.7μm/dm^3 and Pb^{2+} is 1nm/dm^3. It was assumed that the system was in equilibrium with air having a CO_2 fugacity of 370 μ bar [Powell *et al.,* 2009].

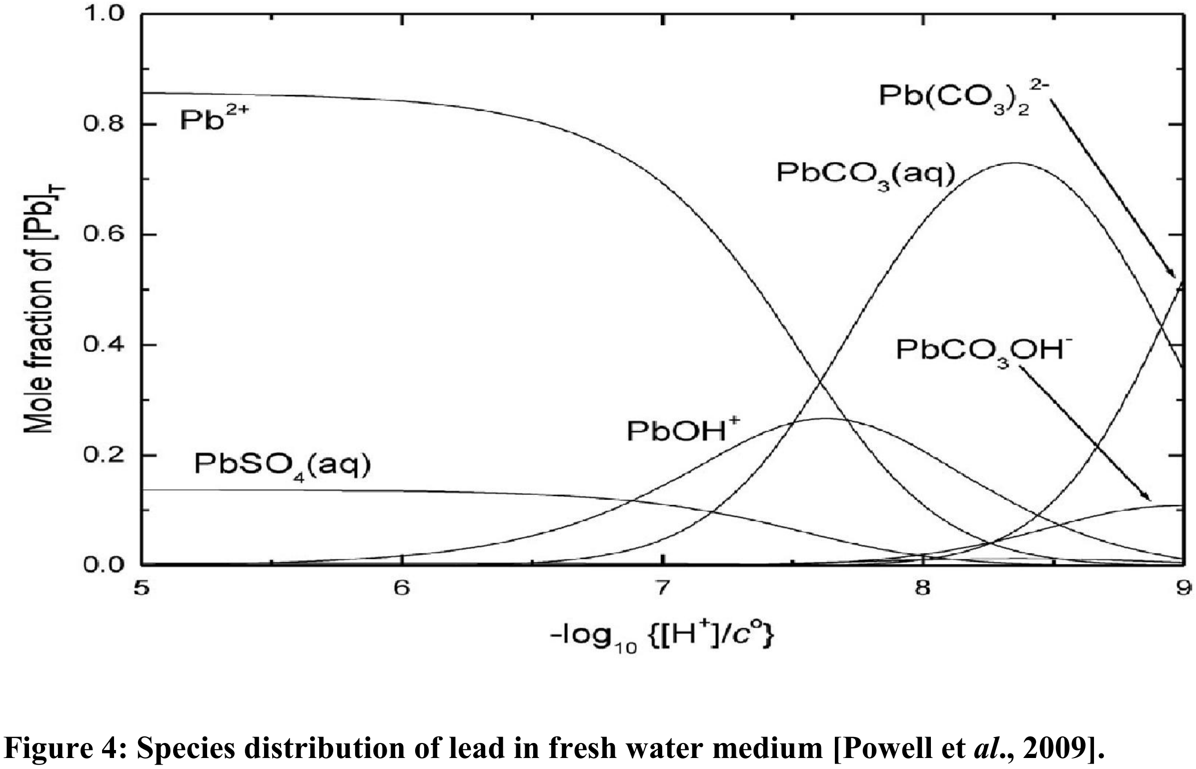

Figure 4: Species distribution of lead in fresh water medium [Powell et *al.*, 2009].

Changes in water chemistry for example declining pH or ionic composition could make sediment of lead to grow into more re-mobilized and potentially bioavailable to aquatic organisms [Weber, 1993]. Lead sorption to bed sediments or suspended organic matter grows with increasing pH, increasing amounts of iron or manganese and with polarity of particulate matter like clay. At higher pH, lead precipitates as $[Pb\ (HCO_3)]^+$ and $[Pb\ (OH)]^+$ into bed sediments [Weber, 1993]. Conversely at lower pH lead is repelled from the adsorbent surface [Gao *et al.,* 2003].

2.4.3 Copper

In surface water, copper may exist in many different chemical species from inorganic salts, free copper ions and organically bound copper [Jones and Bolam, 2007]. Copper speciation in water is influenced by dissolved oxygen, pH, and the presence of oxidizing agents and chelating compounds or ions [U.S.EPA, 1995]. Surface oxidation of copper yields copper (I) oxide or hydroxide. In most cases, copper (I) ion is subsequently oxidized to copper (II) ion. Nevertheless, copper (I) chloride and copper (I) ammonium complexes, when they form, are steady in aqueous solution [WHO, 2004]. Dissolved copper ions are taken away from the solution through sorption to minerals, organic solids and clays or by precipitation. Copper adsorbs to clay materials in a pH- dependent manner, and the presence of particulate organic matter increases adsorption [Barceloux, 1999].

Study was done on eight rivers in Norway, and it was found that pH had the most significant influence on copper speciation. At low pH levels most copper was dissolved while at high pH levels, copper occurred predominantly in particulate or colloidal form. Consequently, in river water of pH 3.1, almost all copper was in dissolved fraction, and at pH range of 6.9-7.2 all the three fractions (dissolved, particulate and colloidal) occurred in significant amounts [Gundersen and Steinnes, 2003]. Cu^{2+} predominates in a carbonate-buffered water system with pH below 6.5. $CuCO_3$ on the other hand, is predominant in the pH extent of 6.5-9.5 that is the pH range of most waters. At pH 7, an increase in alkalinity from 50 to 250 mg/l (as $CaCO_3$) decreases the Cu^{2+} levels from 25 to 9% of the total copper present. These results indicate that copper is more bioavailable and toxic in soft, less alkaline water than in hard, more alkaline water [Kiaune and Singhasemanon, 2011].

2.4.4 Manganese

In the aquatic environment, manganese exists in two main forms namely Mn (II) and Mn (IV). Transition between these two forms takes place through redox reactions that may be abiotic or microbially mediated [Heal, 2001]. Manganese speciation is largely controlled by redox and pH conditions. Mn (II) is predominant at lower redox potential and pH, with an increasing proportion of colloidal manganese oxyhydroxides above pH 5.5 in non- dystrophic waters [CICAD, 2004]. The Mn (II) ion is more soluble compared to Mn (IV); consequently, manganese will tend to become more bioavailable with decrease in redox potential and pH [Heal, 2001]. Studies show that the presence of chlorides, sulphates and nitrates can increase the solubility of manganese and therefore increasing its aqueous mobility and uptake by plants [CICAD, 2004].

A series of oxidation/ precipitation and adsorption occurs when Mn (II) is present in aerobic environment, which eventually renders Mn biologically unavailable as insoluble manganese dioxide [CICAD, 2004]. However, in pH below 8.5 the kinetics of Mn (II) oxidation is slow [Zaw and Chiswell, 1999]. The sequence of reactions that involve the oxidation of Mn (II) and subsequent precipitation of manganese dioxide includes simultaneous occurrence of dissolved Mn (II), Mn (II) adsorbed to particulates, hydrous oxides of Mn (III) and Mn (II) - ligand complexes, with individual concentrations depending on factors that include inorganic carbon, organic carbon, sulphate, chloride, temperature, pH and time [CICAD, 2004].

2.4.5 Zinc

The principle oxidation state of zinc is +2 [Petrucci and Harwood, 1993]. In the case of water solutions, zinc acts as very strong acidic metal that binds halogen ions in series $F^- > Cl^- > Br^- > I^-$. Notably, within pH 6.7, zinc in water is in a divalent state that is available for sorption and thus creates complexes with organic substances [Odobasic, 2012]. Under oxidizing conditions, the Zn^{2+} ion persists up to a pH of 7.8. Above that pH, zinc hydroxides and zinc carbonates predominate. Under more reducing circumstances, the preferred zinc species is ZnS [Bjornsdottir, 1996].

2.4.6 Iron

In aquatic environment, iron can exist in two oxidation states which are iron (II) and iron (III). Iron (II) is the stable form in reducing environments such as low-oxygen sediments, hypolimnetic lake water and ground water. Iron (III) is the stable form in well oxygenated waters [Sjostedt, 2012]. In oxygenated circum-neutral pH water, the oxidation of iron (II) to iron (III) is fast, whereas in more acid water the oxidation is slower [Davison, 1993]. At significant concentrations and in the presence of other ions, iron (II) can precipitate in various mineral forms such as amorphous iron sulphide (FeS), siderite ($FeCO_3$) or vivianite [$(Fe_3 (PO_4).8\ H_2O$] [Sjostedt, 2012].

Iron (III) has a very low solubility; as it easily precipitates as different secondary oxides and hydroxides such as ferrihydrite, hematite [α-Fe_2O_3], goethite [α- FeO (OH)] among others. Iron (III) hydroxides can easily adsorb other ions; this is because of the high surface area and a high amount of functional groups with a pH dependent charge. Iron (III) readily complexes to natural organic matter unlike iron (II). These two features make iron (III) omnipresent in particulate and colloidal form in fresh water [Sjostedt, 2012].

2.5 Chemical Speciation Techniques

Florence [1976] devised the first metal speciation scheme. The scheme divided metals into dissolved and particulate by passing samples through a 0.45µm filter. The dissolved fraction was measured with ASV which distinguished the ASV-labile and non-ASV labile fractions. Samples were irradiated with UV radiation and they were then passed through chelating resins. Since then, many different speciation schemes have been devised [Bjornsdottir, 1996]. Speciation analysis is determined in two ways namely: direct measurement of different forms of the target element in the laboratory and chemical modeling which applies known thermodynamic relationships among chemical forms to predict the overall equilibrium distribution. In many instances, a combination is used when chemical analysis can only determine certain forms and modeling are used to predict the other forms relative to the measured forms. For example, the concentrations of metal ion can be measured in the laboratory by different techniques that include inductively coupled plasma mass spectroscopy (ICP-MS), Graphite furnace atomic absorption spectroscopy (GFAA), Atomic emission spectrometry (AES), neutron activation analysis and X-ray spectroscopy among others. Free metal ion concentrations can be measured using fluorescence method [Zeng *et al*., 2003] and electroanalytical techniques that use microelectrodes [Galceran *et al*., 2007]. Combinations of complex analytical techniques are often required for a direct speciation measurement (beyond total metal or free ion). Chromatographic methods (ion chromatography (IC), liquid chromatography (LC) and gas chromatography (GC) and capillary electrophoresis (CE) are the most popular techniques for separation which are mainly combined with AES, AAS, ICE-AES or ICP-MS in order to carryout speciation. Table1 below shows the most relevant separation methods and hyphenated techniques for metal speciation [Morais *et al*., 2012].

Table 1: The most relevant separation methods and hyphenated techniques for metal speciation [Morais *et al*., 2012].

Technique	Principle	Type of analysis	Applications
Liquid Chromatography (LC)	Repartition of the analyte between Stationary phase and a mobile liquid one.	Simultaneous Multi element Analysis.	-Environmental metal speciation -hyphenated techniques for speciation: LC-AAS, LC-AES, LC-ICP-AES, LC-ICP-MS.
Gas chromatography (GC)	Repartition of the analyte between Stationary phase and a mobile gas one.	Simultaneous Multi element Analysis.	-Volatile or thermally stable compounds (Hg, Sn and Pb alkyl compounds. -Techniques for speciation: GC-AES, GC-AAS and GC-MS.
Ion chromatography (IC)	LC technique which uses ion- exchange Resins.	simultaneous multi element analysis.	-lack of selectivity control; -hyphenated techniques for metal speciation: IC-AAS,IC-ICP-AES, and IC-ICP-MS.
Capillary electrophoresis (CE)	Differential migration of charged analytes along a capillary filled with a suitable conducting electrolyte.	simultaneous multi element analysis.	-cations, organic and inorganic compounds of the same metal, metalloids; - hyphenated techniques: CE-MS,CE-ICP-MS.

Chemical speciation modeling depends strongly on the presumption of equilibrium and on values of equilibrium constants determined experimentally. The models for chemical speciation rely on thermodynamics and mass balance to determine the concentration of every species that comprises a given component. Mass balances are set to be equal to the concentration of every element in the system (commonly measured analytically), and mass action equations are well-defined through equilibrium constants .Thus the mass balances is defined as:

$$M_j = \sum_{j=1}^{N_c} A_{ij}\,\chi_i/\gamma_i \quad \text{.......................................} \quad (1)$$

Where A_{ij} is the stoichiometric coefficient that gives the mole number of component j in species i; Mj is the total mass of component j; γi is the activity coefficient of species i; χi is the activity of the aqueous species i and N_c is the number of components. The mass action equation is defined as:

$$X_i = \beta_i \prod_{J=1}^{N_C} C_j^{A_{ij}} \quad \text{.......................................} \quad (2)$$

β_i represent the total equilibrium formation constant for species i [Vanbriesen *et al.,* 2010].

There are several different geochemical models developed for metal speciation like EQ3NR, WATEQ4F, PHREEQC, Visual MINTEQ, MINTEQA, MINEQL+ and JESS among others. These models are supplied with standard thermodynamic database, including enthalpy values, reaction constants and specific interaction theory parameters for correcting ionic strength or Debye-Huckel functions [Vanbriesen *et al.,* 2010].

A research in Kuwait desert was carried out to investigate geochemical evolution of fresh groundwater and also to reveal the groundwater chemical types and genesis. Chemical speciation was carried out using WATEQ4F program. The main water chemical types were found to be sodium bicarbonate, calcium bicarbonate, sodium chloride, sodium sulphate and calcium sulphate [Hadi and Al-Ruwaih, 2008]. Birsan and Luca [2010] used PHREEQC program to carry out analysis of chemical speciation of heavy metals in surface waters of an area polluted by mining activities. The program allowed the determination of the distribution of studied elements. PHREEQC speciation model was used to carry out speciation of some metal ions in groundwater in Yola. The results based on model calculations indicated the presence of $Ca^{2+,}$ Mg^{2+},K^+ and Na^+ ions [Obiefuna and Orazulike, 2010].

Speciation of heavy metals in water of Qaraauon reservoir was carried out by [Korfali and Jurdi, 2011]. ICP-MS technique was used to determine the total concentration of metals, and AQUACHEM software interfaced to PHREEQC geochemical computer model was used to carry out speciation analysis. The results from speciation data predicted that a high percentage of lead and nickel were present as carbonate complex species and low percentage as free hydrated ions. A greater percentage of zinc was present as carbonate complexes, followed by the free hydrated ion; while highest percentage of cadmium was present in form of free hydrated ion, followed by carbonate complexes. The sensitivity of free hydrated ion of nickel, cadmium and zinc in the reservoir water revealed that zinc and cadmium depended on pH and alkalinity while lead and nickel were only dependent on pH. Chemical analysis and speciation of surface waters was carried out at the historic lights in California using EQ3NR computer program. The results indicated that aqueous manganese and selenium existed as metastable reduced species while copper occurred mainly as cupric carbonate complexes [Kara, 2011]. In Lake Modrac, differential pulse anodic stripping voltammetry (DPASV) was used in the determination and speciation of trace heavy metals. The total concentrations and stable chemical forms were determined using DPASV while software programs MINTEQ, HIDRA and CHEAQES were used to determine the labile chemical forms [Odobasic, 2012]. Kyle *et al.,* [2010] used JESS computer program to carry out speciation of trace metals in gold processing solutions in Australia. The results indicated that at low salinity, lead carbonate was the dominant species below pH 8 and lead hydroxide above pH 8.It was also found that at high salinity, lead remains soluble up to about pH 8, with several lead complexes like chlorides and sulphates being identified. There is still not enough information on element species to understand all processes linked to potential metal toxicity and mobility, especially in Kenya these methods have not been applied in details hence the importance of the current research work.

2.6 Instrumentation

2.6.1 Atomic Absorption Spectrophotometer (AAS)

Atomic absorption spectrophotometer can easily determine the concentration of heavy metals in liquid samples. It uses monochromatic radiation to excite vaporized atoms in their ground state. This instrument consists of a light source cell; a monochromator and a detection system (see Figure 5 below). The light source, which is usually a hollow cathode lamp, emits essentially line radiation of the same wavelength as being absorbed by the element under study [Maiti, 2004].

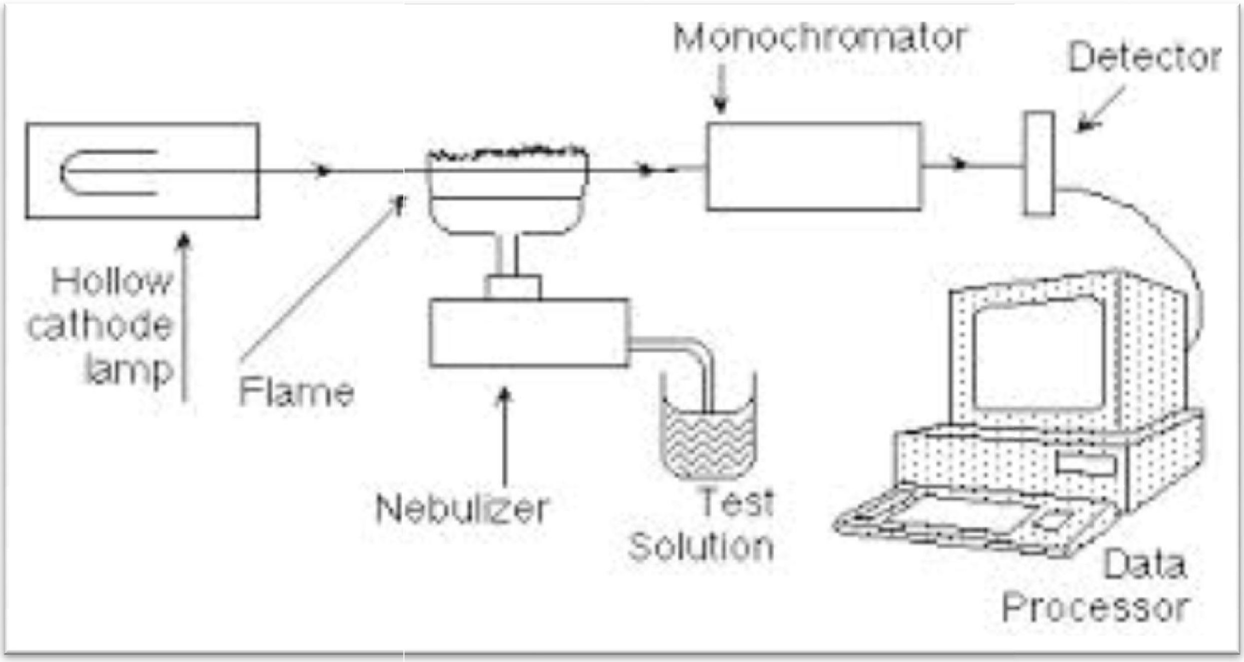

Figure 5: Schematic representation of Atomic Absorption Spectrophotometer [Maiti, 2004].

Atomic absorption spectrophotometer uses a combination of known absorption spectra and measured absorbance to determine the analyte concentration [Melville, 2014]. Beer-Lambert law is used to correlate absorption and concentration of the metal in the sample. Each element has a characteristic absorption spectra relating to specific, quantized transitions of electrons to excited states. The locations of the absorption peaks are unique to each element, and their intensities are directly proportional to the concentration of the sample [Melville, 2014]. In order to measure the electronic transitions, the sample to be analyzed must be atomized using a flame atomizer which employs an air acetylene flame. When aerosols of the analytes are aspirated through the flame, they evaporate fast and leave behind pure particles of the analyte, which are heated into gaseous phase and dissociated into free ions. At this point, additional energy excites the gaseous metal atoms and the specific wavelengths absorbed leave behind characteristic intensities from which concentration can be calculated using the Beer-Lambert law (Equation 3) [Melville, 2014].

$$A = \varepsilon \ell c \qquad (3)$$

Where: A is the absorbance of the solution.

ε is the extinction coefficient, which is a measure of absorptivity of the substance in solution.

ℓ is the distance that light travels through the solution.

c is the concentration of the solution.

Errors can result from sources such as:

Flame temperature- very high temperatures cause ionization of metal atom and thereby decreasing sensitivity, also if the temperature is too low, less metal atoms will be excited and therefore decreasing the sensitivity [Melville, 2014]. Sensitivity can be enhanced by using a small amount of an easily ionizable element which will reduce the creation rate of an analyte.

Impurities- impurities that are present in the sample can create complexes or compounds that are less volatile than the sample. Mitigation of sensitivity loss from chemical interference can be achieved by using a solvent which will vaporize more easily, or by using a hotter flame which will vaporize stabler compounds more readily [Melville, 2014].

2.6.2 UV-Visible spectrophotometer

A UV-Visible spectrophotometer is an instrument that measures the amount of light that is absorbed by coloured solutions. It can determine the absorption spectrum of anions like phosphates, sulphates, nitrites, fluoride among others. For the concentrations of these anions to be determined, one has to colour the sample using specific reagent for each anion. A solution which is more concentrated will absorb more light than a less concentrated one. A spectrophotometer quantitatively measures the absorbance which can be used in the determination of concentration of an absorbing molecule. It operates by passing light from a lamp through a monochromator that separates the light into individual wavelengths. Using an adjustable slit, light of a single wavelength is allowed to get into the sample which is placed in a transparent cuvette. A photoelectric tube which is placed on the other side of the cuvette, measures the amount of light that pass through the sample. Spectrophotometer measures the amount of light transmitted, which can be converted to absorbance [Behera *et al.,* 2012].

The concentration of the unknown solutions can be determined using a spectrophotometer in two ways. The first method is to generate a standard curve which is a graph of absorbance versus concentration for standard solution whose concentrations are known. The absorbances of the unknown solutions are then compared to the standard curve [Behera *et al.,* 2012]. The second method is by using the Beers-Lambert law where the wavelength at which a substance absorbs best (λ_{max}) is determined and a standard curve showing a linear relationship between absorbance and concentration is drawn. Extinction coefficient which is used to find the concentration for that substance under similar instrument conditions can then be calculated [Behera *et al.,* 2012]. Extinction coefficient relates absorbance to concentration using the Beers-Lambert law as shown in Equation 3. With the advancement in technology, most of the spectrophotometers recently determine the concentration of solutions automatically (for example DR 3900 spectrophotometer) and therefore one does not need to follow all these steps. The sources of errors include:

Stray light- this is where radiation emerges from monochromator of all wavelengths other than the bandwidth at the selected wavelength. It may originate from imperfections in the dispersing element or other surfaces, from diffraction effects and other aberrations or from damaged components. Stray light causes apparent negative deviation from Beer-Lambert law.

Wavelength inaccuracy- this is noticed when measurements are taken on the side of an absorbance peak; therefore it is prudent to measure where possible, at the absorbance maximum where the rate change is at minimum.

Noise- there are problems associated electronic noise in the detector and also, noise element associated with the random fluctuations of the photon beam that reaches the detector, which may be apparent in the amplifier output.

CHAPTER 3

MATERIALS AND METHODS

3.1 The Study Area

Nairobi River flows through the Kenyan capital city Nairobi and is the main river of the Nairobi River Basin. It is a complex of several streams that join in the eastern part and confluence the Athi River and then flows into the Indian Ocean. It has several tributaries including Ruiru River, Kamiti River, Karura River, Gitathuru River, Mathare River, Kirichwa River and Ngong River [Ndiritu *et al*., 2003]. The source of Nairobi River is Ondiri swamp in Kikuyu Township, whereby farmers residing around the swamp use the swamp water to irrigate crops, for domestic purposes as well as for livestock. Downstream from the catchment, there is change from subsistence farming into residential estates. In some instances, raw sewage from the residential estates is discharged into the River. As the River cuts across the central part of the city, it passes through areas of commercial activities. The River also passes through the areas reserved for industrial establishments where some of them discharge waste waters into existing municipal sewerage system and or into the River [Makathimo and Guthiga, 2010].

In this study, six sampling points which belong to the tributary of Nairobi River were selected. These sampling points were Chiromo Kirichwa Kubwa (1),Kirichwa Ndogo (2) Kileleshwa Kirichwa Kubwa (3), Lenana School (4), Lenana dam (5) and Riara (6). This tributary confluence the Nairobi River at the Museum Hill Bridge as shown in Figure 6. Table 2 below shows the coordinates of the sampling points.

Table 2: The coordinates of the sampling points of the study area.

Sampling point	Longitude	Latitude	Altitude
Chiromo Kirichwa Kubwa (1)	036.8094^{o}E	01.275033^{o}S	5538 ft
Kirichwa Ndogo (2)	036.780133^{o}E	01.2795^{o}S	5748 ft
Kileleshwa Kirichwa Kubwa (3)	036.8077^{o}E	01.2744^{o}S	5337 ft
Lenana School (4)	036.7358^{o}E	01.29965^{o}S	5952 ft
Lenana dam (5)	036.766717^{o}E	01.2992167^{o}S	5959 ft
Riara (6)	036.774367^{o}E	01.295833^{o}S	5787 ft

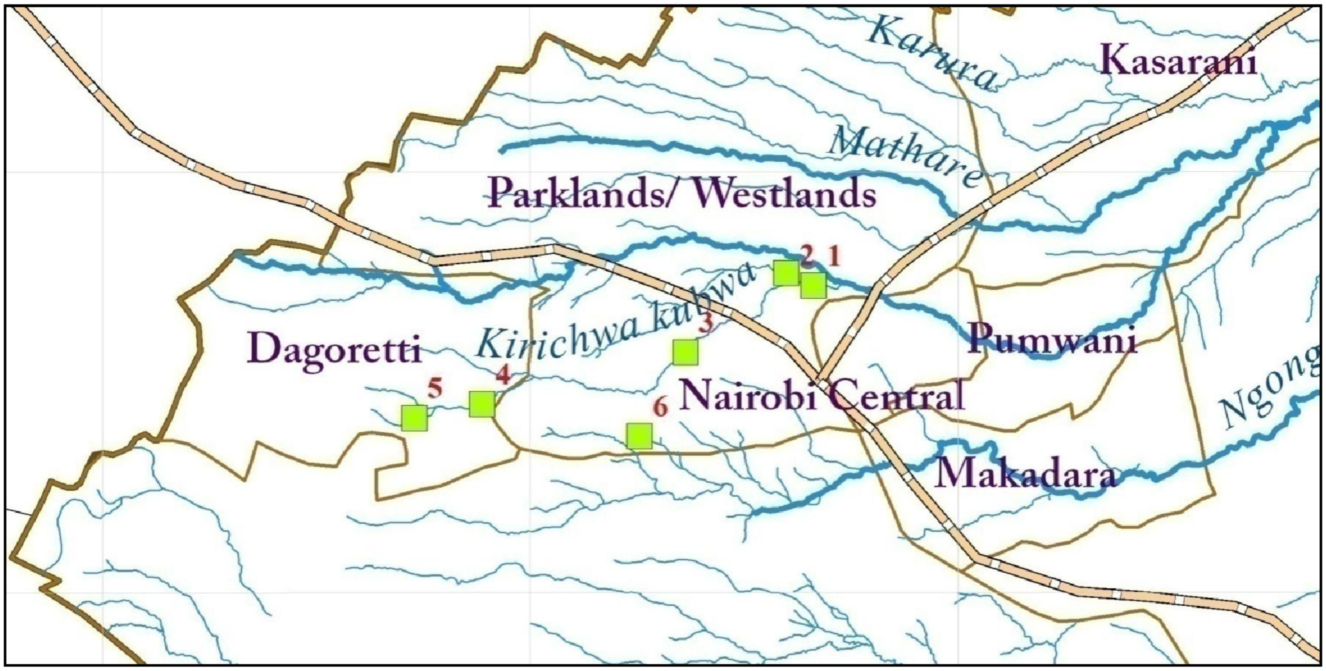

Figure 6: A map showing the sampling points. Source: Stanley Atonya, Geology Department, University of Nairobi.

3.1.1 Description of the Sampling points

Chiromo Kirichwa Kubwa (sampling point 1) (Figure 7) is located at the University of Nairobi behind the school of Biological sciences complex at Chiromo campus. This point receives water that flows through the National arboretum (botanical garden devoted to trees). From this point, the river confluences Chiromo Nairobi River near the Museum Hill Bridge.

Figure 7: Chiromo Kirichwa Kubwa (sampling point 1).

Kirichwa Ndogo (sampling point 2) is located near Lavington estate. There were potted plants near the sampling point during the time of sampling.

Kileleshwa Kirichwa Kubwa (sampling point 3) (Figure 8) is located near a petrol station and a car wash where small scale businesses including carpentry are carried out. Residential houses are also constructed near this sampling point. All these may contribute to the quality of water in the river.

Figure 8: Kileleshwa Kirichwa Kubwa (sampling point 3).

Lenana School (sampling point 4) (figure 9) and Lenana dam (sampling point 5) (figure 10) are located in Lenana School where cultivation takes place in the school farm and also there was a pig farm near the dam. Effluents from the teacher's quarters, school laboratories and students dormitories might get their way into the river.

Figure 9: Lenana School (sampling point 4).

Figure 10: Lenana dam (sampling point 5).

In Riara (sampling point 6) (Figure 11), most of the pollution may be as a result of domestic effluents from the residential houses constructed near the river, and also from dumpsite located at Naivasha road (Figure 3).

Figure 11: Riara (sampling point 6).

3.2 List of Chemicals, Reagents, Equipments and their Sources

Chemicals and reagents: Potassium chromate (May and Baker ltd, Dagenham, England), silver nitrate (Loba chemie ltd, Mumbai, India), sodium chloride (British Drug House chemicals ltd, Poole, England), SPADNS reagent, COD digestion reagent, Sulfaver 4 sulphate reagent, Nitriver 3 nitrite reagent, Molybdate and amino acid reagents for phosphate, fluoride, nitrite, phosphate and sulphate standard solutions (Hach company, U.S.A), lead, copper, chromium, manganese, zinc and iron standard solutions (Merck, Darmstadt, Germany), nitric acid (Riedel-dehaen, Germany).

Equipments: Atomic Absorption Spectrophotometer (AAS) model AA- 6300 (Shimadzu, Japan) UV-Visible spectrophotometer model DR 3900 (Hach company, U.S.A), BOD incubator model DNP 9022 (Shanghai, China), EC/TDS/NaCl/Temp/pH meter model MI 306 (Apps Enterprises ltd, Australia), Dissolved Oxygen meter model HI 9146 (Hanna, U.S.A).

3.3 Sample Collection

Sampling was carried out in the different locations (Figure 5) once during the wet season (December 2013) and once during the dry season (July 2013). December is usually a dry month however in this study, it is considered a wet season because of delay in rains which started towards the end of November. At each the sampling point, 2L and 1L plastic containers (cleaned and rinsed before) were rinsed twice with water sample before a sample was collected. The sampling containers were fully submerged in the water surface and filled slowly so as to collect a representative sample and also to avoid disturbance of the sediments. The samples were collected in duplicate and concentrated nitric acid was added to water samples (in 1L container) for metal analysis in order reduce the water pH to less than 2 and to preserve the water samples. The pH, conductivity, TDS and temperature were measured by dipping the portable EC/TDS/NaCl/Temp/pH meter directly in the river as soon as the samples were collected.

Dissolved oxygen was also determined by dipping a dissolved oxygen meter into the river. The water samples were then transported to the laboratory and preserved at a temperature of 4^oC while waiting for analysis. All the reagents that were used were of analytical grade, and the experiments were performed in triplicate for accurate analysis.

3.4 Determination of Biochemical Oxygen Demand (BOD)

A pair of 50 mL of the water samples from each sampling point was measured and the dissolved oxygen level (mg/L) of each sample recorded immediately using a dissolved oxygen meter. The second water sample from each sampling point was placed in an incubator in complete darkness at 20^oC for 5 days after which the dissolved oxygen reading (mg/L) was made. The BOD level (mg/L) was then determined by subtracting 5th day reading from 1st day reading.

3.5 Determination of the Chemical Oxygen Demand (COD)

The chemical oxygen demand was determined using reactor digestion method. 100 mL of the water sample from each sampling point was homogenized for 30 seconds; the COD reactor was turned on and preheated to 150^oC. 2.00 mL of each sample was pipetted into the vials containing the COD digestion reagent; the blank was prepared by pipetting 2.00 mL of distilled water into the vial containing the COD digestion reagent. The vials containing the samples and the blank were capped tightly, swirled to mix and placed in the preheated COD reactor to heat for two hours. The vials were then removed from the reactor and inverted several times while still warm and they were left to cool to room temperature after which colorimetric determination of COD was carried out using a UV-Visible spectrophotometer with wavelength of 620nm. The blank was used to zero the spectrophotometer after which the sample vial was placed in the cell holder, and the results were read in mg/L COD [Hach, 2004].

3.6 Determination of the Total Suspended Solids (TSS)

Water samples homogenized and 100 ml filtered through pre-weighed Whatman filter paper. The residue retained in the filter paper was dried in an oven at 105°C for one hour. TSS was calculated as the weight of the residue per volume of the sample filtered, and the result was expressed in mg/L.

3.7 Determination of the Anions

3.7.1 Sulphate

Sulfaver 4 turbidimetric method was used in the determination of sulphate. The sulphate ions in the sample react with Barium in the sulfaver reagent to form insoluble barium sulphate. The amount of turbidity formed is directly proportional to the sulphate concentration [Hach, 2004]. Solutions of 10, 20,30,40,50, 60 and 70 mg/L SO_4^{2-} were prepared by appropriate dilution of 1000 mg/L sulphate standard solution. These solutions, together with sulfaver 4 sulphate reagent were used to calibrate the UV-Visible spectrophotometer. A clean sample cell was filled with 10 mL of the sample, followed by contents of one sulfaver 4 reagent powder pillows and swirled to mix. The blank was prepared by filling one sample cell with 10 mL of distilled water and contents in one sulfaver 4 reagent pillow; this was used to zero the spectrophotometer. The sample was placed into the cell holder and the results were read in mg/L SO_4^{2-} [Hach, 2004].

3.7.2 Phosphate

Amino acid method was used in the determination of Phosphate. Solutions of 2, 4, 6 and 8 mg/L were prepared by appropriate dilution of 10 mg/L of phosphate standard solution. These solutions together with molybdate and amino acid reagents were used to calibrate the UV-Visible spectrophotometer. A 25 mL mixing cylinder was filled with 25 mL of the sample followed by 1.00 mL of molybdate reagent using 1.00 mL calibrated dropper. 1.00 mL of amino acid reagent solution was then added and inverted several times to mix (this was the prepared sample).A spectrophotometer with wavelength 530nm was allowed to run for 10 minutes, after which it was zeroed using the blank. The prepared sample was then placed into the sample cell holder, and the results were read in mg/L PO_4^{3-} (Hach, 2004).

3.7.3 Nitrite

Diazotization method was used in the determination of nitrite. Solutions of 1, 2 and 3 mg/L together with Nitriver 3 nitrite reagent were used to calibrate the UV-Visible spectrophotometer. 10.0 mL of the sample was put into a round sample cell followed by contents in one Nitriver 3 nitrite reagent powder pillow. The spectrophotometer was allowed to run for 20 minutes at a wavelength of 607nm. A pink color developed if nitrite was present. Another sample cell was filled with 10.0 mL of the sample (this was the blank), and it was used to zero the spectrophotometer. The prepared water sample was then placed into the cell holder, and the results were read in mg/L NO_2—N (Hach, 2004).

3.7.4 Fluoride

SPADNS method was used in the determination of fluoride. Fluoride combines with part of the zirconium in the SPADNS reagent to form a colorless complex which bleaches the red color in an amount that is proportional to the fluoride concentration [Hach, 2004]. The UV-Visible spectrophotometer was calibrated using 0.5, 1.0, 1.5 and 2.0 mg/L of fluoride standard solution, together with SPADNS reagent. 10.0 mL of the water sample was pipetted into a dry round sample cell and 10.0 mL of distilled water was pipetted into a second dry sample cell (this was the blank). 2.0 mL of SPADNS reagent was pipetted into sample cells containing the sample and the blank. The spectrophotometer was allowed to run for 1 minute at a wavelength of 570nm. The blank was used to zero the spectrophotometer. The prepared water sample was placed into the cell holder, and the concentrations of fluorides were read in mg/L (Hach, 2004).

3.7.5 Chloride

The reagents for the determination of chloride concentration were prepared as follows:

Potassium chromate solution: 50 g of neutral potassium chromate was dissolved in 50.0 mL of distilled water; silver nitrate was then added to the solution to produce slight red precipitate and was left to stand for one night after which, it was filtered and the resulting filtrate diluted to one litre volume with distilled water.

Silver nitrate solution: 2.4 g of silver nitrate was dried at 105^0C and dissolved in one litre of distilled water.

Sodium chloride solution: 16.48 g of NaCl was dried at 105^0C and dissolved in one litre of distilled water, this was the stock solution. Working solution was prepared by diluting 100 mL of stock solution to one litre with distilled water.

Silver nitrate was standardized by placing 25.0 mL of diluted NaCl solution in one evaporating dish and adding 25.0 mL of distilled water. 50.0 mL of distilled water was added to another evaporating dish, and 1.00 mL of chromate solution was added to each dish. $AgNO_3$ solution was placed in the burette and added drop by drop to the NaCl solution in one of the dishes until reddish brown color was observed. The amount of $AgNO_3$ used was recorded and corrected for error due to the increase in volume of NaCl solution resulting from the addition of $AgNO_3$. For this correction dilution factor was subtracted which is (0.003× volume of $AgNO_3$ at the end of titration) +0.02. 50 mL of the sample was placed in one volumetric flask and 50 mL of the distilled water in another conical flask. 1.00 mL chromate solution was added to each volumetric flask, standardized $AgNO_3$ solution in the burette was added to the sample drop by drop until reddish coloration appeared, compared with the original color of the distilled water and chromate mixture in the second conical flask. The amount of $AgNO_3$ solution used was recorded, and this procedure was repeated for all the water samples, and the amount of chlorides (mg/L) was calculated as follows: mL of ($AgNO_3$-0.2) ×7.1/ml of the sample taken [NCWSC, 2009].

3.8 Determination of the Concentration of Heavy Metals

Solutions of 0.50, 1.00, 1.50, 2.00, 2.50, 3.00, 3.50, 4.00, 4.50 and 5.00 mg/L were prepared by appropriate dilution of 1000 mg/L of each metal ion solution. These were used to calibrate the Atomic Absorption Spectrophotometer. 100 mL of well mixed samples for Cr, Cu, Pb, Fe, Zn and Mn were transferred into respective beakers; 5.00 mL of nitric acid was added to each beaker and each covered with a watch glass, after which the prepared water samples were placed in a hot plate. Boiling chips were added to the samples in the hot plate to avoid acid boiling and minimize spatter. The samples were brought to slow boiling and evaporated to 10.0 mL. The water samples were then left to cool to room temperature. Distilled water was added to 10.0 mL of the sample to make 100 mL. The levels of Pb, Mn, Zn, Cu, Fe and Cr in the worked- up samples were then profiled using flame Atomic Absorption Spectrophotometer (AAS).

3.9 Speciation Analysis

Speciation analysis was carried out using the Joint Expert Speciation System (JESS) thermodynamic program (version 7.3) [May and Murray, 2008]. JESS has extensive data at multiple ionic strengths, temperature and background electrolytes. This program contains coded knowledge about chemical speciation and about the way chemical speciation calculations should be performed. JESS operates with input files in which calculation instructions are arranged according to key words which are largely self instructive. The input parameters were temperature, pH and concentrations of Pb, Mn, Cu, Fe, Zn, Cr, NO_2^-, Cl^-, F^- and SO_4^{2-}; which were used to carry out speciation analysis. Program TELSUB, which sets up a default model for equilibrium calculation was executed, followed by programs DOSUB, DOLGK, DOBAS and

DOQED in sequence. These programs transform the relevant thermodynamic data, taken from the JESS Parent Database into the equations which are finally solved (by DOQED). Lastly, program VEWQED was executed where speciation of specified heavy metals and the anions was displayed. The speciation distribution was determined in terms of concentration and percentage abundance of each species based on the total concentrations of the components.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 *In-situ* Measurements

The pH values for this study were observed to be slightly higher during the dry season (7.04-7.77) as compared to the wet season (6.89-7.67) (Figure 12). Slightly lower pH values during the wet season were attributed to higher temperatures (Figure 13). According to [CWT, 2004], increasing temperatures decreases the pH of water. The pH also decreases with increase in rainfall [Atobatele *et al.,* 2008]. High pH values at Kirichwa Ndogo were attributed to fertilizers from the potted plants near the sampling point. Effluents containing acid from the car wash and garage could have resulted to lower pH values at Kileleshwa Kirichwa Kubwa during the dry season. At each sampling point, the pH values were within the acceptable KEBS and NEMA limits for natural water (6.5-8.5).

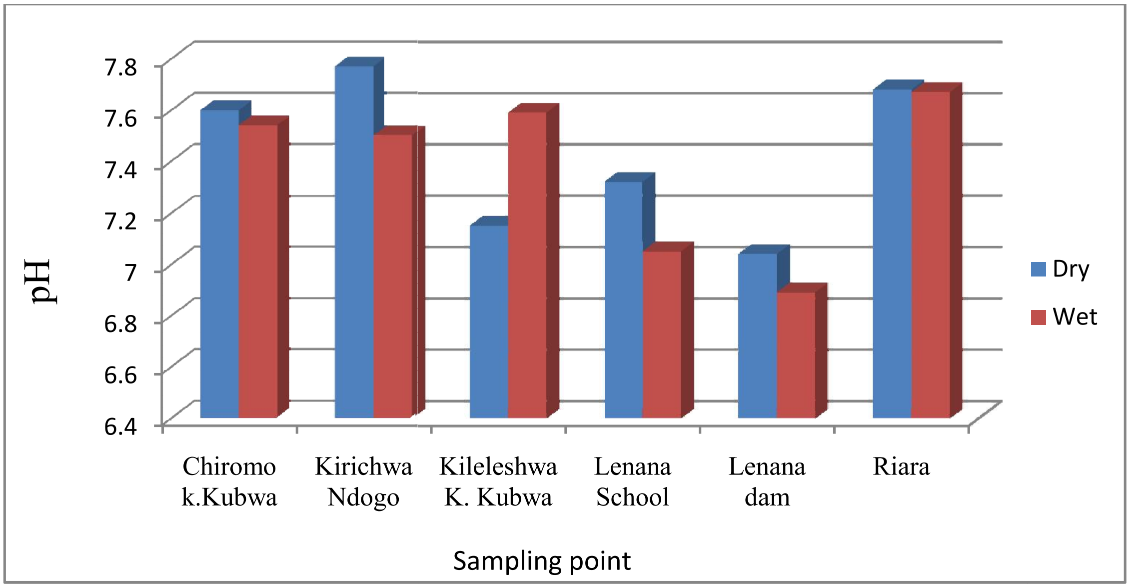

Figure 12: The pH of water samples recorded during the dry and wet season.

The temperature values were observed to be slightly lower during the dry season (18.3-20.4°C ±0.05°C) as compared to the wet season 19.2- 25.0⁰C ±0.05°C) (Figure 13). For the dry season, sampling was carried out in the evening on July which is normally a cold month hence low temperatures, compared to that of the wet season where sampling was carried out at around mid morning on December which is a hot month. Kirichwa Ndogo recorded the highest temperature of 25°C during the wet season; this is because sampling at that point was carried out at around mid day.

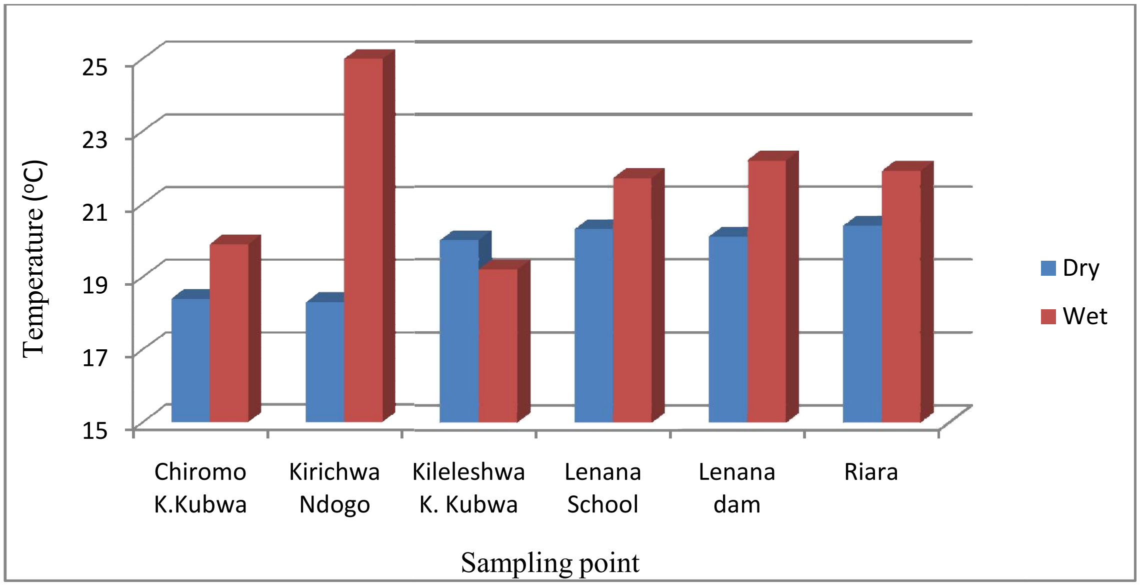

Figure 13: Temperature values (°C) recorded during the dry and wet season.

The values of electrical conductivity were found to be significantly higher during the wet season as compared to the dry season (Figure 14). This possibly came from runoff of ionic species which carries a lot of dissolved conducting minerals into the river water. The conductivity range was 348-861µS/cm and 450-881µS/cm during the dry and wet seasons, respectively (Figure 14). This shows that there were a lot of dissolved conducting substances in the river. The electrical conductivity values were above the WHO limits of 600µS/cm for natural water at Lenana School and Riara during both dry and wet seasons and Kileleshwa Kirichwa Kubwa during the wet season; a factor which was attributed to domestic effluent discharges into the river which increased the concentration of the ions. Similar observation was also made by Khalik *et al.,* [2013]. The presence of Schools with pollution loadings near Riara and Lenana School could have also led to high electrical conductivity values at these sampling points. Conductivity values at Lenana dam are low because of increased volume of water at the dam. High conductivity values (above 600μS/cm) indicate pollution load of the river.

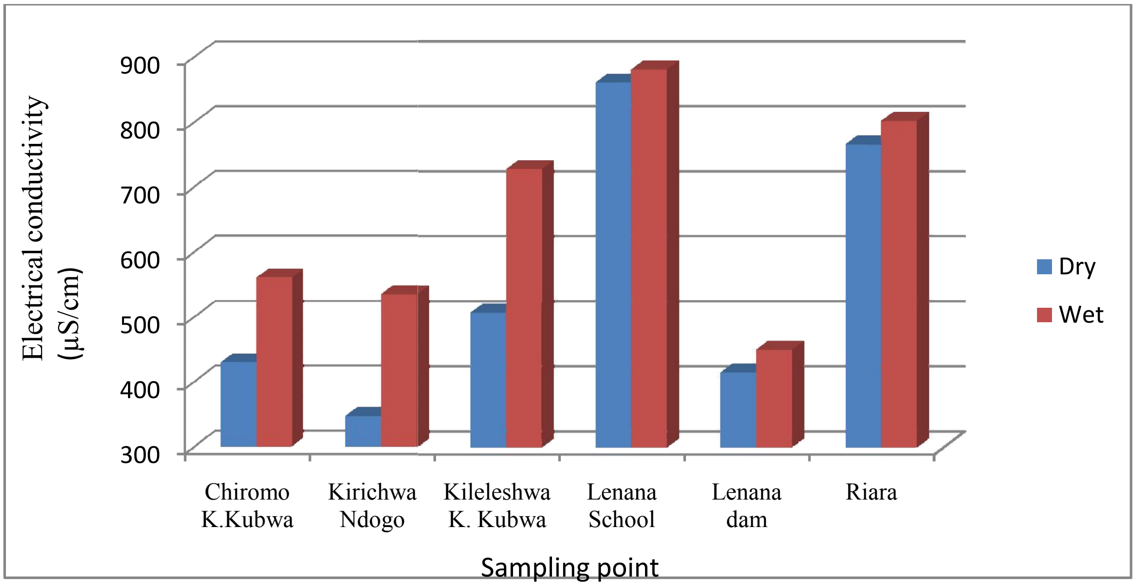

Figure 14: Electrical conductivity values (μS/cm) recorded during the dry and wet season.

The trend for total dissolved solids (TDS) values was similar to that observed for electrical conductivity. This is expected, since most dissolved solids in water are ionic species which tend to increase electrical conductivity. Therefore TDS values are expected to increase with increased electrical conductivity. TDS values were below the acceptable NEMA limits of 1200 mg/L for domestic water and the range was 176-431mg/L and 197-438 mg/L during the dry and wet seasons, respectively (Figure 15). High TDS values recorded during the wet season was attributed to surface runoff, and relatively higher concentration of anions like sulphates, phosphates and chlorides. The highest concentration of TDS was obtained at Lenana School during the wet season (438 mg/L). This might be due to runoff or leachate which carries pollutant with dissolved minerals from the school farm into the river. Domestic effluents from the teacher's quarters might have also contributed to high TDS values at that sampling point. Like electrical conductivity, low TDS values recorded at Lenana dam may be attributed to increased volume of water. The proximity of Lenana School and Riara to schools with pollution loading could have contributed to relatively high TDS values at these sampling points. TDS is not a health hazard although high levels may indicate hard water which may lead to scale build up in pipes and aesthetic problems such as salty or bitter taste in water.

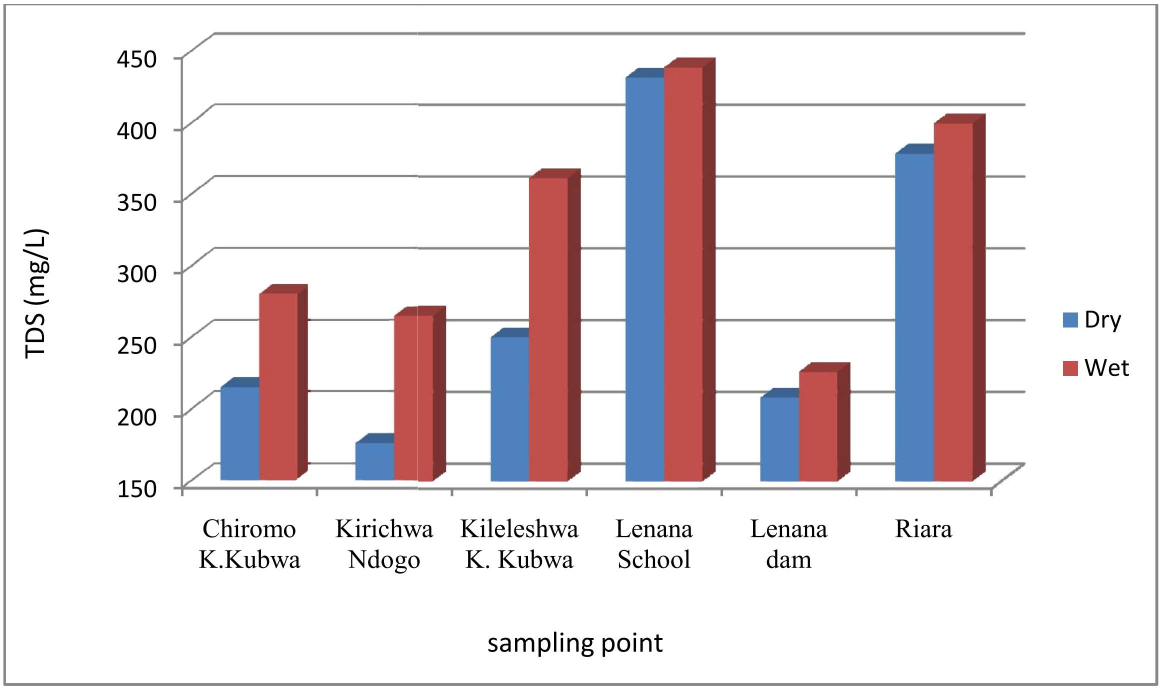

Figure 15: Concentration of TDS (mg/L) recorded during the dry and wet season.

The dissolved oxygen concentrations were found to be higher during the wet season, as compared to the dry season (Figure 16). This is probably due to increased volume of water during the wet season hence high aeration due to turbulence brought about by storm water. During the dry season, the water volume was less so there was minimal aeration and therefore less dissolved oxygen in the water. This is also due to the fact that the BOD levels were relatively high during the dry season as compared to the wet season; the higher the BOD level, the more rapidly oxygen is depleted thereby resulting to low DO levels. The dissolved oxygen concentration range was 8.10-14.80 mg/L and 17.23-22.72 mg/L during the dry and wet seasons, respectively. These values are accepted by the World Health Organization; since the minimum level of dissolved oxygen in drinking water should be 4 mg/L.

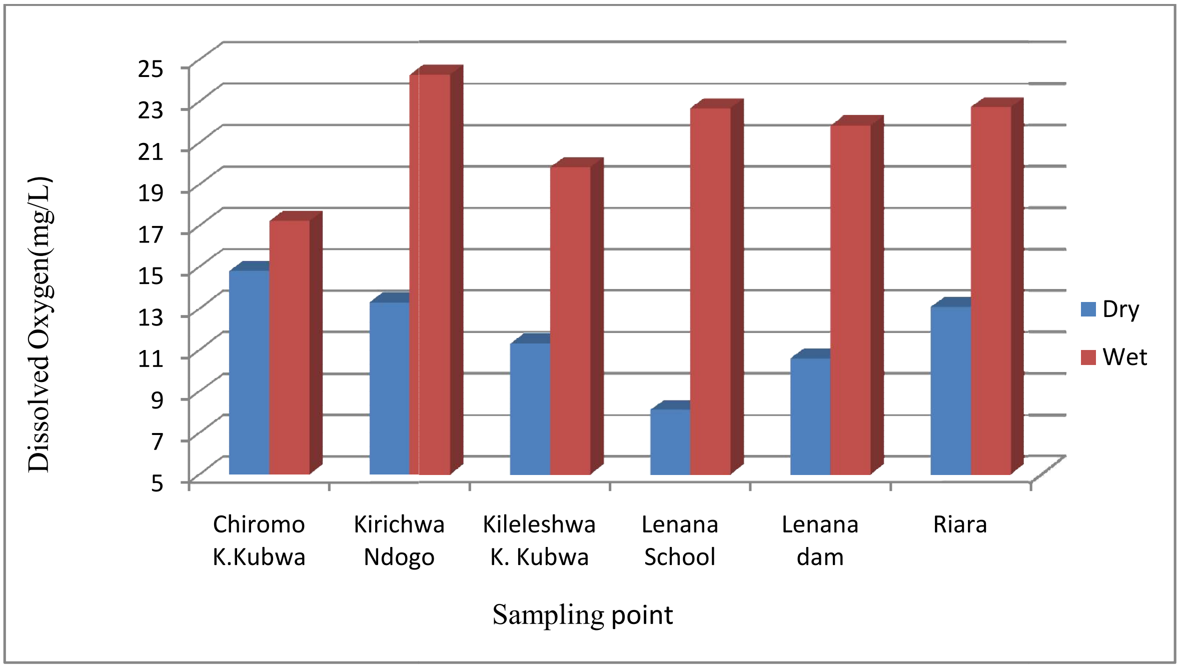

Figure 16: Dissolved Oxygen values (mg/L) recorded during the dry and wet season.

4.2 Laboratory Analysis

4.2.1 Total Suspended Solids (TSS)

The concentration of total suspended solids was observed to be significantly higher during the wet season as compared to the dry season (Figure 17). This was attributed to runoff which carries particles into the river during the wet season. Lenana dam recorded very high TSS values compared to other sampling points during the wet season; this was attributed to ploughing which had been carried out in the school farm. Lenana School contained the least concentration of TSS which was as a result of vegetation that reduced soil erosion into the river. All the sampling points were exposed to particle pollutant since TSS concentrations were above the NEMA recommendation of 30 mg/L for effluent discharge.

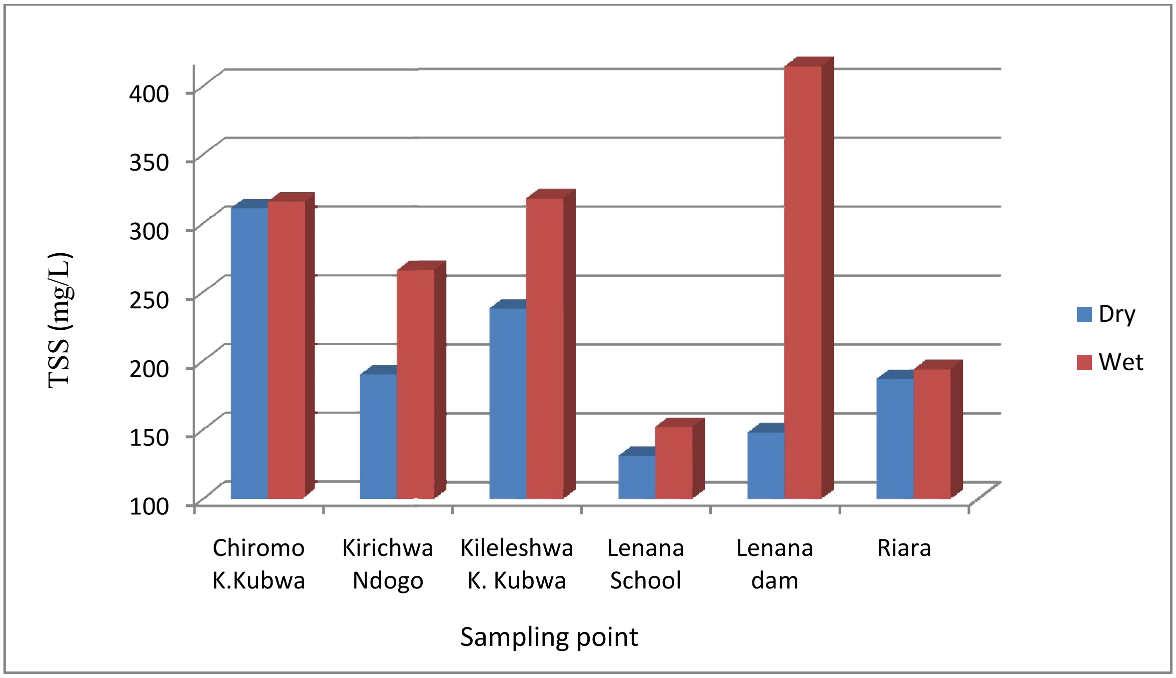

Figure 17: The level of TSS (mg/L) recorded during the dry and the wet season.

4.2.2 Biochemical Oxygen Demand (BOD)

The Biochemical Oxygen Demand concentration recorded in this study was found to be slightly higher during the dry season as compared to the wet season (Table 3). This was attributed to dilution of water during the wet season. High levels of BOD recorded at Lenana dam and Kirichwa Ndogo was attributed to chemical usage of fertilizers from the School farm and the potted plants. At Riara sampling point, a high BOD level was attributed to domestic discharge effluents. The values of BOD for both seasons were found to be below the NEMA limit of 30 mg/L for effluent discharge.

Table 3: The levels of BOD (mg/L) recorded during the dry and wet season.

Sampling point	Chiromo Kirichwa Kubwa	Kirichwa Ndogo	Kileleshwa Kirichwa Kubwa	Lenana school	Lenana dam	Riara
Wet season	16.27 ±0.01	21.80 ±0.01	14.27 ±0.015	10.93 ±0.018	22.91 ±0.021	22.79 ±0.02
Dry season	19.76 ±0.014	25.26 ±0.015	22.25 ±0.016	15.52 ±0.022	24.30 ±0.019	25.16 ±0.01

4.2.3 Chemical Oxygen Demand (COD)

The concentration of chemical oxygen demand was found to be higher during the dry season (90-730 mg O_2/L) as compared to the wet season (40-410 mg O_2/L); this might be attributed to a higher concentration of chemical species because of reduced volume of water during the dry season. However, Lenana dam and Kirichwa Ndogo recorded higher concentration during the wet season rather than the dry season (Figure 18). Lenana School recorded the highest concentration (730 mg/L) of COD during the dry season; this might be due to animal waste from the pig farm in the School; since the most substances oxidized by dissolved oxygen is organic matter having biological origin like dead plants and animal wastes. Similar observation was made by Choudhary *et al.,* [2011]. The COD levels in all the sampling points except Chiromo Kirichwa Kubwa during the wet season were above the NEMA limits of 50 mg/L for effluent discharge. Relatively lower levels of COD at Chiromo Kirichwa Kubwa indicate the presence of less organic substances as compared to other sampling points.

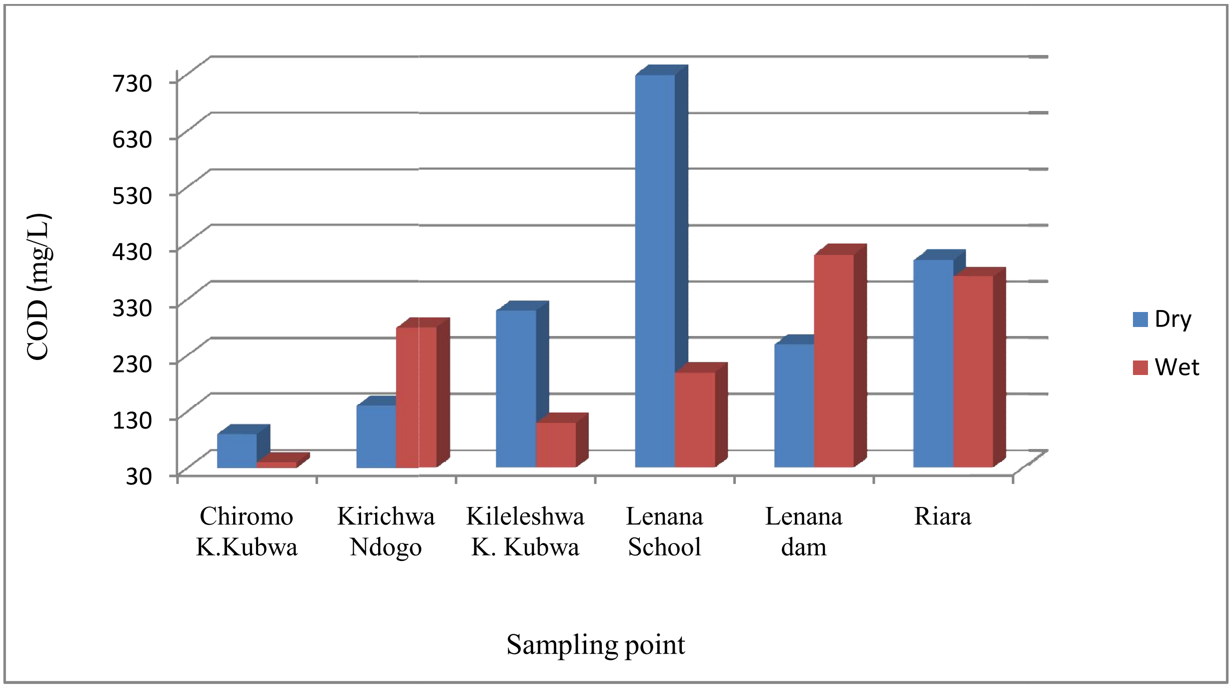

Figure 18: The levels of COD (mg/L) recorded during the dry and the wet season.

4.2.4 Phosphate

The concentration of phosphates in this study increased during the wet season rather than in the dry season. The high levels of phosphates during the wet season could be attributed to the high rate of decomposition of organic matter and from surface runoff. Chiromo Kirichwa Kubwa and Lenana School recorded the highest values during the wet and dry seasons respectively (Table 4), these values are above the WHO recommended value of 5 mg/L for natural water. The high concentrations at Lenana School might be due to surface runoff as farming activities occurred during both seasons or due to use of detergents. While the source of phosphates is usually attributed to the use of fertilizers, man-made sources such as domestic discharges especially use of phosphate-based detergents in households for laundry [Swamy *et al*., 2013] or even changes in land use in areas where phosphorus is naturally abundant in the soil also contributes to phosphates in the water.

Table 4: The total concentration of phosphate (mg/L) recorded during the dry and wet season.

Sampling point	Chiromo Kirichwa Kubwa	Kirichwa Ndogo	Kileleshwa Kirichwa Kubwa	Lenana School	Lenana dam	Riara
Dry season	0.03 ±0.001	0.23 ±0.0021	0.06 ±0.002	5.11 ±0.0022	0.14 ±0.001	0.22 ±0.0023
Wet season	5.96 ±0.003	1.19 ±0.0035	2.33 ±0.004	5.92 ±0.01	4.38 ±0.0173	2.55 ±0.01

4.2.5 Sulphate

The concentration of sulphates was found to be much higher during the wet season as compared to the dry season. This might be attributed to surface runoff from soils containing minerals that are rich in sulphate. Similar observations were made by Swamy *et al.,* [2013]. Sulphate was not detected in Lenana dam during the dry season. This might be due to self-purification process taking place in the dam, and also, there could be no point source. The dam also recorded the least value of sulphate (6 mg/L) during the wet season (Table 5). Riara recorded the highest concentration of sulphate (68 mg/L) during the wet season, which might be attributed to a point source for example household wastes like detergents. Use of fertilizers could have led to relatively high values of sulphate at Kirichwa Ndogo. There is no health-based guideline value recommended for sulphate, however intake of high sulphate levels has gastrointestinal effects.

Table 5: The total concentration of sulphate (mg/L) recorded during the dry and wet season.

Sampling point	Chiromo Kirichwa Kubwa	Kirichwa Ndogo	Kileleshwa Kirichwa Kubwa	Lenana School	Lenana dam	Riara
Dry season	14.0 ±0.0361	16 ±0.012	14.0 ±0.0173	1.00 ±0.01	0.00 ±0.00	3.00 ±0.01
Wet season	37.0 ±0.017	39 ±0.01	36.0 ±0.00	35.0 ±0.0173	6.00 ±0.0012	68 ±0.01

4.2.6 Fluoride

The concentration of fluoride was significantly higher during the wet season as compared to the dry season. This might be due to surface runoff from areas where soils contain fluorides. The fluoride concentration was above the NEMA guideline value of 1.5 mg/L for domestic water and effluent discharge into the environment in Riara, Lenana School and Lenana dam during both dry and wet seasons and in Kirichwa Ndogo during the wet season (Table 6). High concentrations of fluoride at Lenana dam and Lenana School might be due to contamination by fertilizers, animal wastes and effluents containing tooth paste. Similar observations were made by Jason and Christina [2012]. Contamination of fluoride at Kirichwa Ndogo might be attributed to the fertilizers from the potted plants near the sampling point. Concentration of fluoride above 1.5 mg/L carry an increasing risk of dental fluorosis, and much higher concentrations lead to skeletal fluorosis.

Table 6: The total concentration of fluoride (mg/L) recorded during the dry and wet season.

Sampling point	Chiromo Kirichwa Kubwa	Kirichwa Ndogo	Kileleshwa Kirichwa Ndogo	Lenana school	Lenana dam	Riara
Dry season	0.66 ±0.01	0.81 ±0.03	0.39 ±0.01	1.81 ±0.01	1.54 ±0.036	1.18 ±0.01
Wet season	1.47 ±0.062	1.86 ±0.02	0.95 ±0.01	2.87 ±0.055	2.54 ±0.017	2.21 ±0.03

4.2.7 Chloride

The concentration of chloride was observed to be higher during the wet season rather than the dry season (Table 7). This might be attributed to surface runoff from soils contaminated by chlorides.

Table 7: The total concentration of chloride (mg/L) recorded during the wet and dry season.

Sampling point	Chiromo Kirichwa Kubwa	Kirichwa Ndogo	Kileleshwa Kirichwa Kubwa	Lenana school	Lenana dam	Riara
Dry season	0.071 ±0.02	0.0144 ±0.014	0.0426 ±0.012	0.0142 ±0.01	0.0284 ±0.017	0.0285 ±0.021
Wet season	0.886 ±0.026	0.5396 ±0.015	0.5254 ±0.022	0.1846 ±0.018	0.0852 ±0.01	0.2556 ±0.013

Anthropogenic sources of chlorides include livestock wastes, human sewage and synthetic fertilizers [WHO, 2003]. Chloride concentration increased tremendously at Chiromo Kirichwa Kubwa during the wet season, which may be attributed to human wastes and salt which might have been disposed after salting fast food like chips since the second sampling was carried out soon after the graduation ceremony at the University of Nairobi. There is no health- based guideline value that is recommended for chloride in drinking-water; however, chloride concentrations in excess about 250 mg/L can give rise to a detectable taste in water [WHO, 2003].

4.2.7 Nitrite

The concentration of nitrites was observed to be higher during the wet season as compared to the dry season (Table 8). Its concentration in all the sampling points was below the NEMA guideline of 3 mg/L for domestic water which is believed to cause methaemoglobinaemia in infants.

Table 8: The total concentration of nitrite (mg/L) recorded during the wet and dry season.

Sampling point	Chiromo Kirichwa Kubwa	Kirichwa Ndogo	Kileleshwa Kirichwa Kubwa	Lenana School	Lenana dam	Riara
Dry season	0.125 ±0.005	0.057 ±0.007	0.373 ±0.004	0.002 ±0.001	0.002 ±0.0011	0.279 ±0.013
Wet season	0.556 ±0.0072	0.004 ±0.001	0.553 ±0.002	0.048 ±0.001	0.308 ±0.004	0.585 ±0.003

Riara recorded the highest concentration of nitrites during the wet season; this might be attributed to refuse dump runoff which might have led to increased amounts of nitrates which was later reduced to nitrites.

4.3 HEAVY METALS

4.3.1 Iron

During the period of study, iron in the water samples remained above the critical limit of 0.3 mg/L for domestic water [KEBS, 1996] in all the sampling points except Kirichwa Ndogo and Riara during the wet season and Kileleshwa Kirichwa Kubwa during the dry season (Table 9). Iron is profuse in the earth's crust and has many uses industrially, that is probably the reason as to why it was present in relatively high quantities in all the sampling points.

Table 9: The total concentration of iron (mg/L) recorded during the dry and wet season.

Sampling point	Chiromo Kirichwa Kubwa	Kirichwa Ndogo	Kileleshwa Kirichwa Kubwa	Lenana School	Lenana dam	Riara
Dry season	0.4971 ±0.00445	0.3157 ±0.00205	0.0974 ±0.0011	3.1438 ±0.0188	0.9673 ±0.00121	1.2629 ±0.00459
Wet season	0.3270 ±0.005	0.1539 ±0.001	0.5627 ±0.006	1.0388 ±0.005	2.8663 ±0.0012	0.2982 ±0.0011

4.3.2 Manganese

The concentration of manganese was higher during the dry season rather than the wet season in all the sampling points except Kileleshwa Kirichwa Kubwa (Table 10). This might be attributed to the dilution of water during the wet season. The difference in Kileleshwa Kirichwa Kubwa might have been due to runoff from the nearby garage, for example through dry-cell batteries dumped near the river. Riara recorded the highest concentration of manganese during both dry season (3.6843 mg/L) and wet season (1.2577 mg/L). This might be attributed to wastewater discharges containing disinfectants and bleaching agents from the residential houses constructed close to the river. The concentration of manganese in all the sampling points with the exception of Kileleshwa Kirichwa Kubwa during the dry season and Kirichwa Ndogo during the wet season was above the KEBS limits of 0.1 mg/L for domestic water (Table 10). This is a point of concern since high concentrations of manganese have been shown to have health effects such as liver damage, neurotoxicity, chronic respiratory inflammation and birth defects (like cleft lip, heart defects, imperforate anus and deafness).

Table 10: The total concentration of manganese (mg/L) recorded during the wet and the dry season.

Sampling point	Chiromo Kirichwa Kubwa	Kirichwa Ndogo	Kileleshwa Kirichwa Kubwa	Lenana School	Lenana dam	Riara
Dry season	0.5557 ±0.0012	0.1577 ±0.0015	0.0092 ±0.001	2.0644 ±0.0022	1.5393 ±0.001	3.6843 ±0.002
Wet season	0.4475 ±0.001	0.0405 ±0.001	0.7795 ±0.002	0.4514 ±0.001	1.1651 ±0.0011	1.2577 ±0.001

4.3.3 Copper

The concentration of copper was higher during the wet season as compared to the dry season (Table 11). This might be attributed to persistence of copper complexes in the sediments. These dissolved when the volume of water increased during the rainy season and therefore, were detected in the water. Since the concentration of copper was relatively low in all the sampling points and below the NEMA recommendation of 1.0 mg/L for effluent discharge into the environment, its source was attributed to mineralogy and weathering. Similar observation was made by Krishnamoorthy and Nagajaran [2013].

Table 11: The total concentration of copper (mg/L) recorded during the wet and the dry season.

Sampling point	Chiromo Kirichwa Kubwa	Kirichwa Ndogo	Kileleshwa Kirichwa Kubwa	Lenana School	Lenana dam	Riara
Dry season	0.0399 ±0.0014	0.0100 ±0.00	0.0050 ±0.002	0.0150 ±0.004	BDL	BDL
Wet season	0.1799 ±0.001	0.1526 ±0.0012	0.1460 ±0.0007	0.1412 ±0.0017	0.1350 ±0.0006	0.1407 ±0.0005

4.3.4 Zinc

The concentration of zinc was higher during the wet season as compared to the dry season (Table 12). This might be due to surface runoff from soils that may contain natural traces of zinc or dissolution of zinc from the sediments. Its concentration of in all the sampling points was found to be below the NEMA limit of 1.5 mg/L for domestic water and 0.5 mg/L for effluent discharge into the environment. Leachate from fertilizers and insecticides, urban runoff and municipal sewage are the main sources of zinc in waters [Usha and Vikram, 2012]. Since the concentration of zinc in this study was very low, its source was attributed to mineralogy and weathering.

Table 12: The total concentration of zinc (mg/L) recorded during the wet and the dry season.

Sampling point	Chiromo Kirichwa Kubwa	Kirichwa Ndogo	Kileleshwa Kirichwa Kubwa	Lenana school	Lenana dam	Riara
Dry season	0.0192 ±0.00221	BDL	BDL	BDL	BDL	BDL
Wet season	0.0197 ±0.013	BDL	0.0179 ±0.0016	0.0042 ±0.0003	0.0064 ±0.0007	BDL

4.3.5 Lead

Lead was detected in Chiromo Kirichwa Kubwa and Kileleshwa Kirichwa Kubwa during the dry season and in Kileleshwa Kirichwa Kubwa, Lenana School and Lenana dam during the wet season (Table 13). In all these sampling points, the concentration of lead was above the NEMA limit of 0.05 mg/L for domestic water and 0.01 mg/L for effluent discharge into the environment. Kileleshwa Kirichwa Kubwa recorded the highest concentration of lead during both seasons, which might be attributed to effluents from the garage and car wash situated close to the river. The high concentration of lead obtained during the wet season might be attributed to the surface runoff from a point source. For example, lead present at Lenana School and Lenana dam during the wet season might be attributed runoff of lead from paint since the school buildings had been renovated during the period for the second sampling.

Table 13: The total concentration of lead (mg/L) recorded during the wet and the dry season.

Sampling point	Chiromo Kirichwa Kubwa	Kirichwa Ndogo	Kileleshwa Kirichwa Kubwa	Lenana School	Lenana dam	Riara
Dry season	0.018 ±0.002	BDL	0.0629 ±0.0011	BDL	BDL	BDL
Wet season	BDL	BDL	0.4415 ±0.0014	0.03626 ±0.0023	0.0474 ±0.001	BDL

4.3.6 Chromium

Chromium was not detected during the wet season, a factor which was attributed to the dilution of water. It was detected in Chiromo Kirichwa Kubwa (0.0846 mg/L), Lenana School (0.0329 mg/L) and Lenana dam (0.0752 mg/L) during the dry season. The concentration of chromium in Chiromo Kirichwa Kubwa and Lenana dam was above the KEBS provisional guideline value of 0.05 mg/L for natural water. The source of chromium at Lenana School and Lenana dam might be attributed to effluents containing detergents.

4.4 JESS RESULTS

4.4.1 Sulphate

According to speciation results over 90% of total sulphates did not form compounds with any metal in all the sampling points except Lenana dam during the wet season, and Riara and Lenana School during the dry season (Figures 19 and 20). This might be attributed to the high concentration of sulphates and low concentration of heavy metals at these sampling points and therefore only small percentage of sulphates formed compounds with metals and the rest were free. Speciation of sulphates at Lenana dam during the wet season is different from other sampling points, this is because the concentration of sulphates is low (6.0 mg/L) and that of iron and manganese are high and therefore more sulphates formed compounds with Fe and Mn.

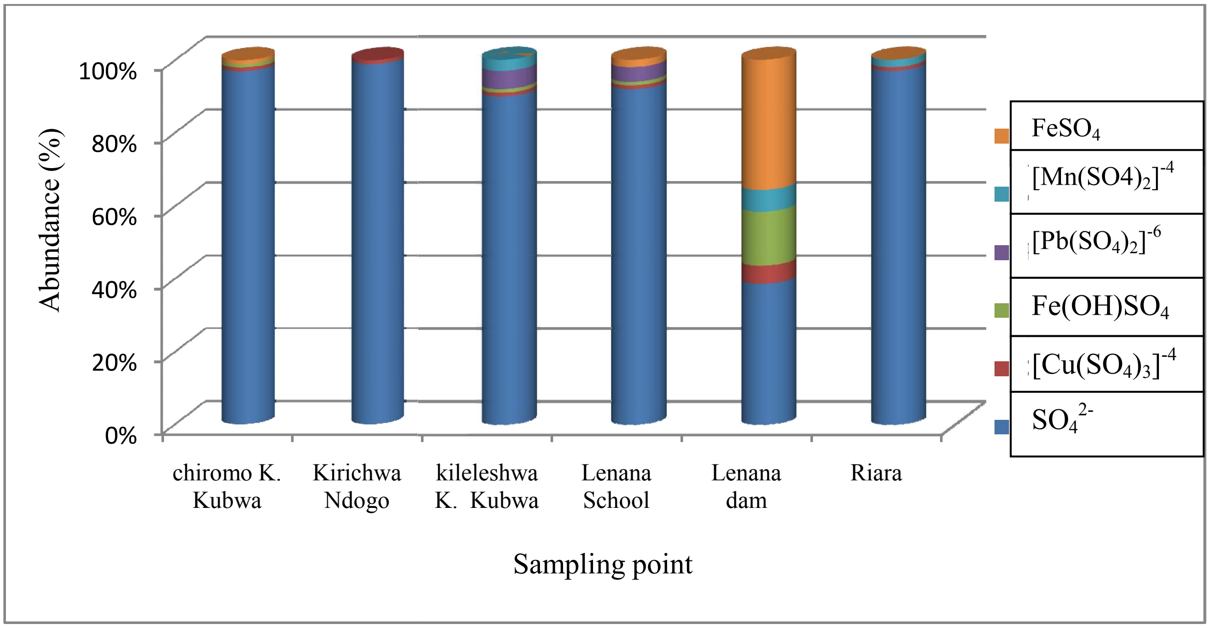

Figure 19: Percentage abundance of sulphates obtained during the wet season.

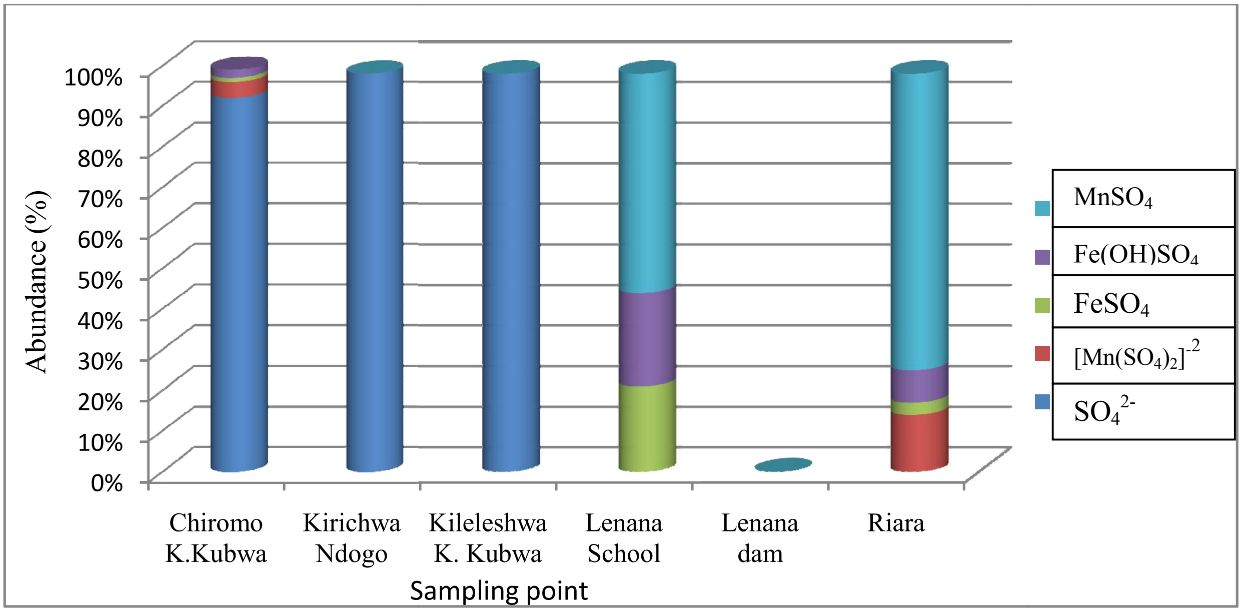

Figure 20: Percentage abundance of sulphates obtained during the dry season.

All sulphates formed compounds with manganese and iron in Riara, and Lenana School during the dry season (Figure 20), a factor which was attributed to high concentrations of both manganese and iron which reacted with the available sulphates.

4.4.2 Fluoride

Over 90% of total fluoride formed compounds with manganese in all the sampling points except Kileleshwa Kirichwa Kubwa (10%) during the dry season (Figure 22) and kirichwa Ndogo (11 %) during the wet season (Figure 21); these sampling points recorded the least concentration of manganese (<0.05 mg/L) which might be the reason as to why small percentage of manganese fluoride complexes was formed. The high percentage of free fluoride (54%) recorded at Kirichwa Ndogo during the wet season might be attributed to low concentration of heavy metals at that sampling point and only small amount could react with the available metals to form compounds.

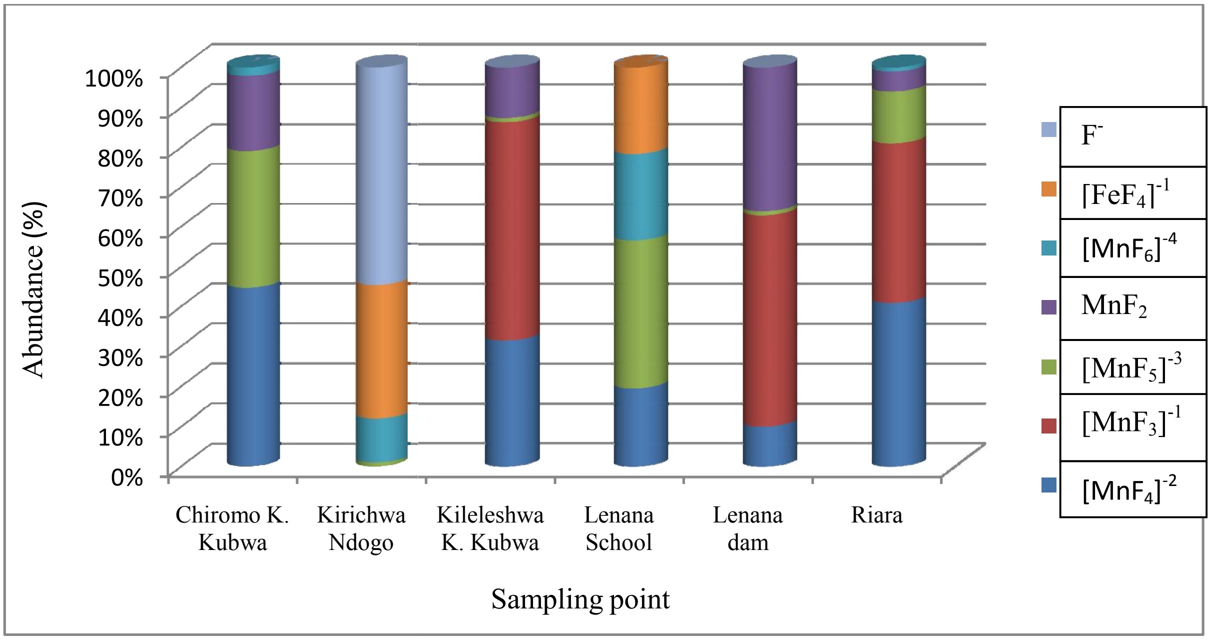

Figure 21: Percentage abundance of fluorides obtained during the wet season.

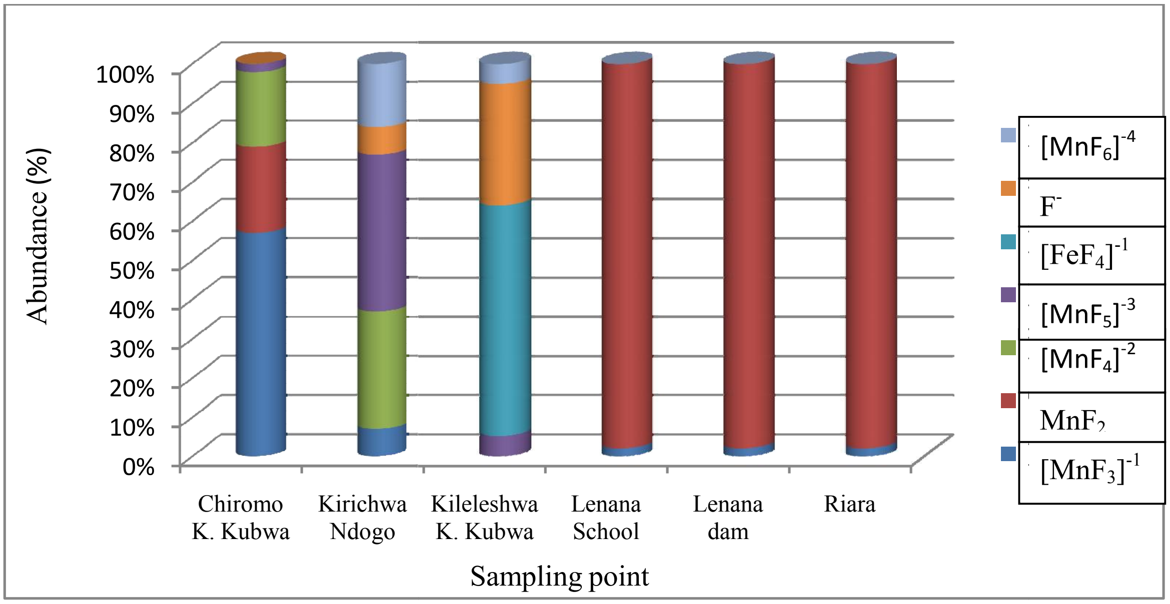

Figure 22: Percentage abundance of fluorides obtained during the dry season.

The higher percentage abundance of $[FeF_4]^{-1}$ at Kileleshwa Kirichwa Kubwa during the dry season was attributed to the higher concentration of iron compared to all the other heavy metals and therefore most fluoride (57%) was coupled to iron.

4.4.3 Chloride

Over 99% of total chlorides were free in all the sampling points except Lenana School, Lenana dam and Riara during the dry season (Figures 23 and 24) where over 60% of total chlorides formed compounds with manganese and iron, a factor which was attributed to high concentrations of both iron and manganese at these sampling points. Small percentage of free chloride recorded at Lenana School (16%) Lenana dam (21%) and Riara (40%) during the dry season was attributed to the small concentration of chloride at these sampling points compared to other sampling points and therefore most chlorides formed compounds with metals. This would explain the difference in speciation pattern at these points (Figure 24). Speciation of chlorides at Lenana dam during the wet season is different from other sampling points; this is because the concentration of iron is relatively high and that of chloride is low and therefore $[FeCl]^{+1}$ was formed.

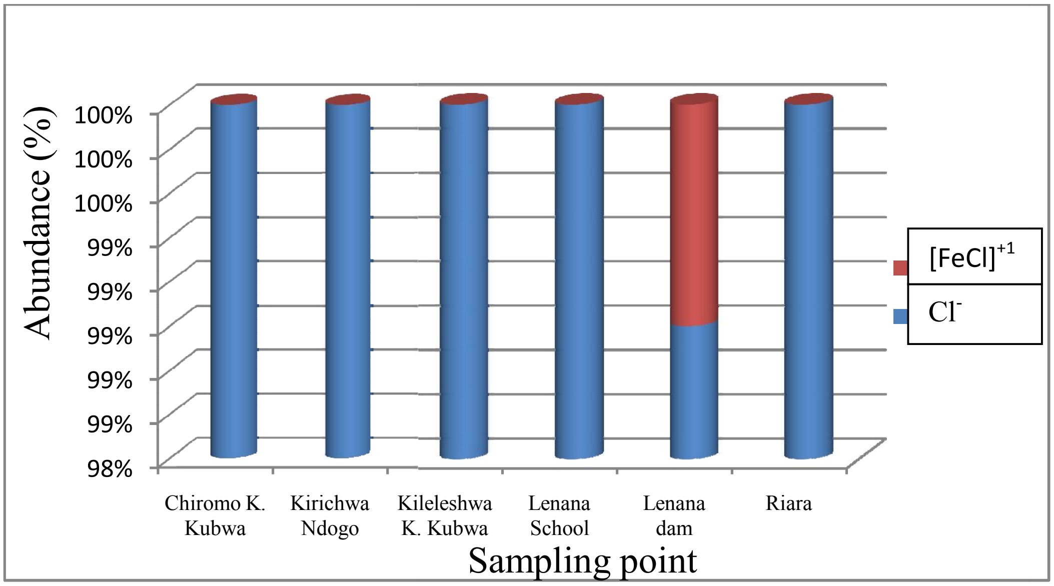

Figure 23: Percentage abundance of chlorides obtained during the wet season.

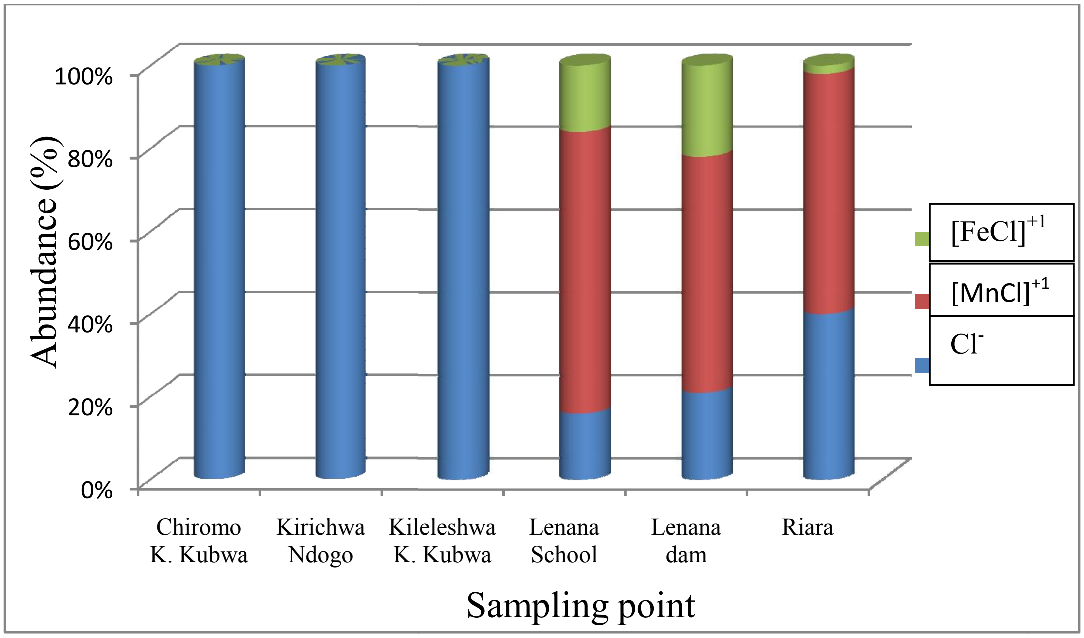

Figure 24: Percentage abundance of chlorides obtained during the dry season.

4.4.4 Nitrite

100% of nitrites were free in all the sampling points during the wet season and in Chiromo Kirichwa Kubwa, Kileleshwa Kirichwa Kubwa and Kirichwa Ndogo during the dry season (Figure 25). This was attributed to low concentration of nitrites, therefore, only small portion formed compounds with metals. The speciation pattern is quite different at Riara, Lenana School and Lenana dam sampling points during the dry season, where by nitrites are coupled with the manganese in very significant proportions. This may be attributed to the high levels of total manganese in the samples from these point and relatively low concentrations of nitrites resulting to domination of the $[MnNO_2]^{+1}$ species at these points.

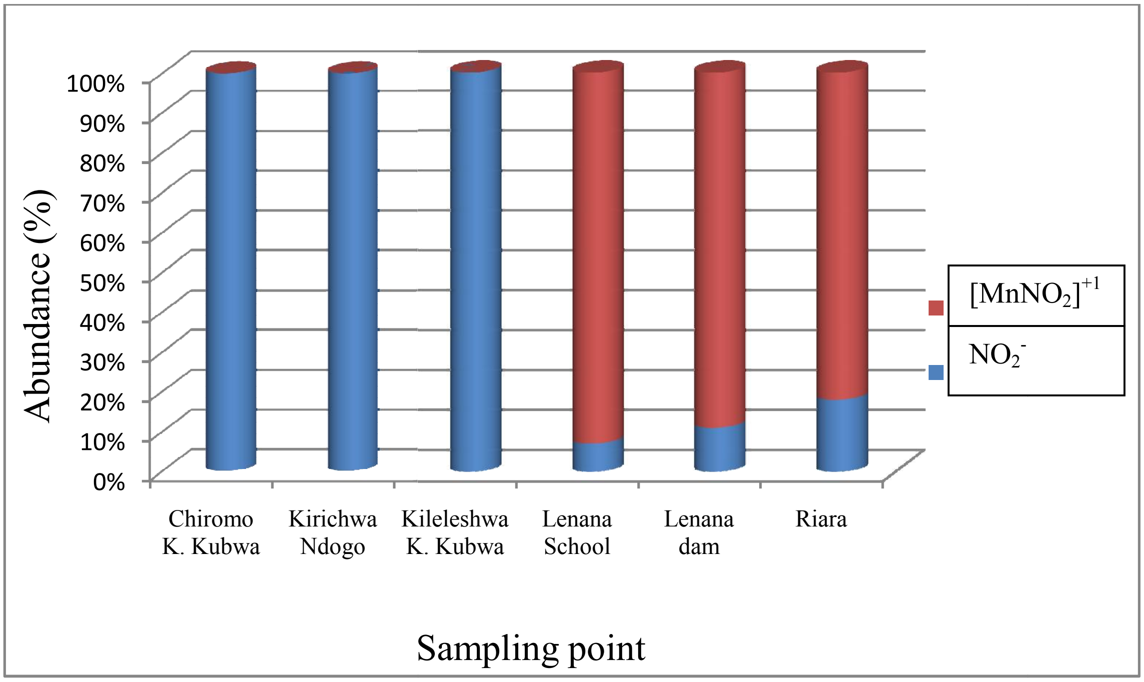

Figure 25: Percentage abundance of nitrites obtained during the dry season.

4.4.5 Iron

The chemical speciation of iron indicated that 69.8% was in oxidation state III, the rest being of oxidation state II. The 30.2% of iron that is in oxidation state II may be attributed to relatively low dissolved oxygen levels. The species of iron in oxidation state III were sulphates, fluorides and hydroxides (Figures 26 and 27). Other major species of iron that were present during the dry season were $Fe(OH)_3$ in Riara (23%), Lenana School (21%) and Lenana dam (9%) and $[Fe(OH)_4]^{+1}$ in Riara (25%), Lenana School (10%) and Lenana dam (2%). The speciation in Kirichwa Ndogo during the wet season is remarkably different from the other sampling points since the fluoride species of iron $[FeF_4]^{-1}$ dominates. This is most probably because of the high fluoride concentration (Table 6) and low iron concentration (Table 9) at that sampling point. The reactive F^- ion reacts with all the available iron in the sampling point and thus, $[FeF_4]^{-1}$ dominates. The scenario changes during the dry season when the concentration of iron increases and fluoride concentration decreases, and the domination of fluorides is taken over by the hydroxyl-sulphate species which is the highest at that sampling point during the dry season. During the dry season, the free Fe^{2+}ion was present in substantial quantities at Lenana School (0.4582 mg/L) and Lenana dam (0.4699 mg /L). These values are above the maximum recommended value for total iron in natural water by the KEBS. This is most probably because the anion concentrations (fluorides, sulphates, nitrites and chlorides) are generally low at these two sampling points, and also the lower amount of dissolved oxygen (Figure 10). The predominance of Fe^{2+} ion at Lenana dam may also be attributed to the absence of sulphate ions at that sampling point (Table 5). Generally the free ion is more toxic than the chemically bonded ion. While the general outlook may show that iron is above the KEBS limit with all the implications of iron toxicity, the speciation results point at the free iron (II) ion. This gives a wholistic indication of the toxicity of the water. The predominance of $[FeF_4]^{-1}$ in Kileleshwa Kirichwa Kubwa during the dry season can be attributed to higher concentration of fluoride and relatively low concentration of iron at that sampling point. The sampling point also has high sulphate ion concentration (Table 5) which would explain the presence of sulphate and hydroxyl-sulphate species. The presence of $[Fe(OH)_2]^{+1}$ at Lenana School, Lenana dam and Riara during the dry season is due to low concentrations of sulphate at these sampling points. Iron sulphate compounds predominated during the wet season (80.6%) as compared to dry season (39.6%). This might be attributed to the high concentration of sulphate during the wet season. Most of the iron formed sulphate complexes possibly due to the fact that the concentration of sulphate was higher than all the other anions and also because of the pH of water which might have favored formation of sulphates. It is worth noting that while the chloride speciation analysis suggests the presence of the chloride species of iron (Figures 19 and 20), this species is not visible in the iron speciation, most probably because the fluoride ion is much more reactive than the chloride ion and thus it dominates.

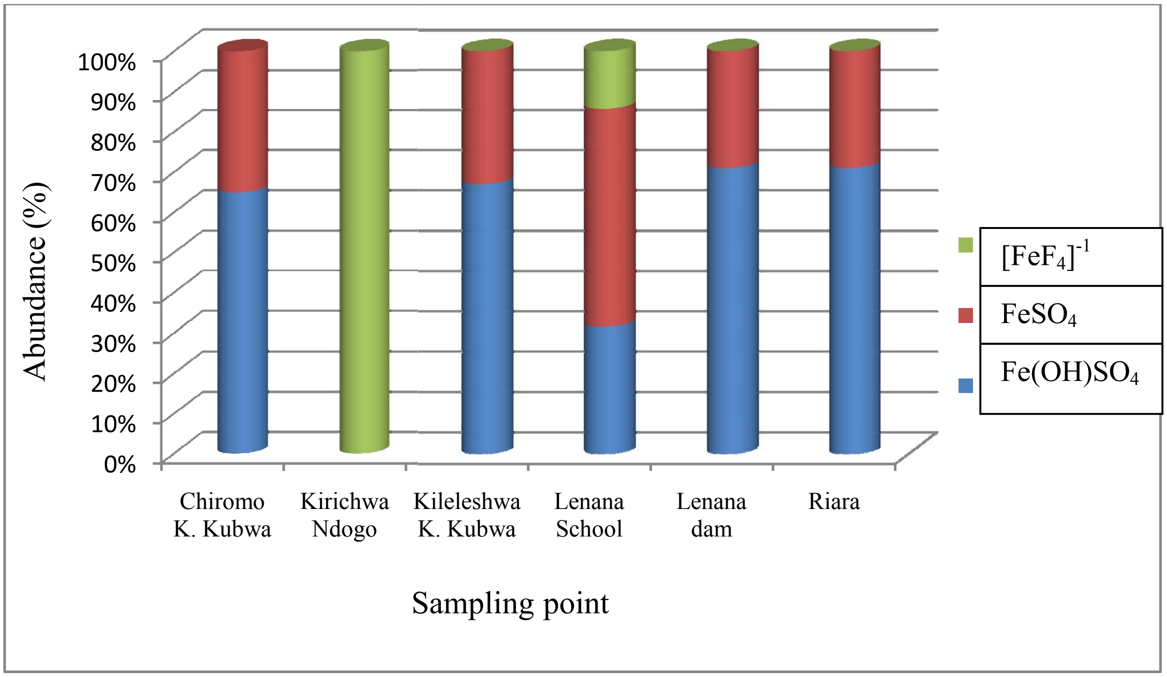

Figure 26: Percentage abundance of major iron species obtained during the wet season.

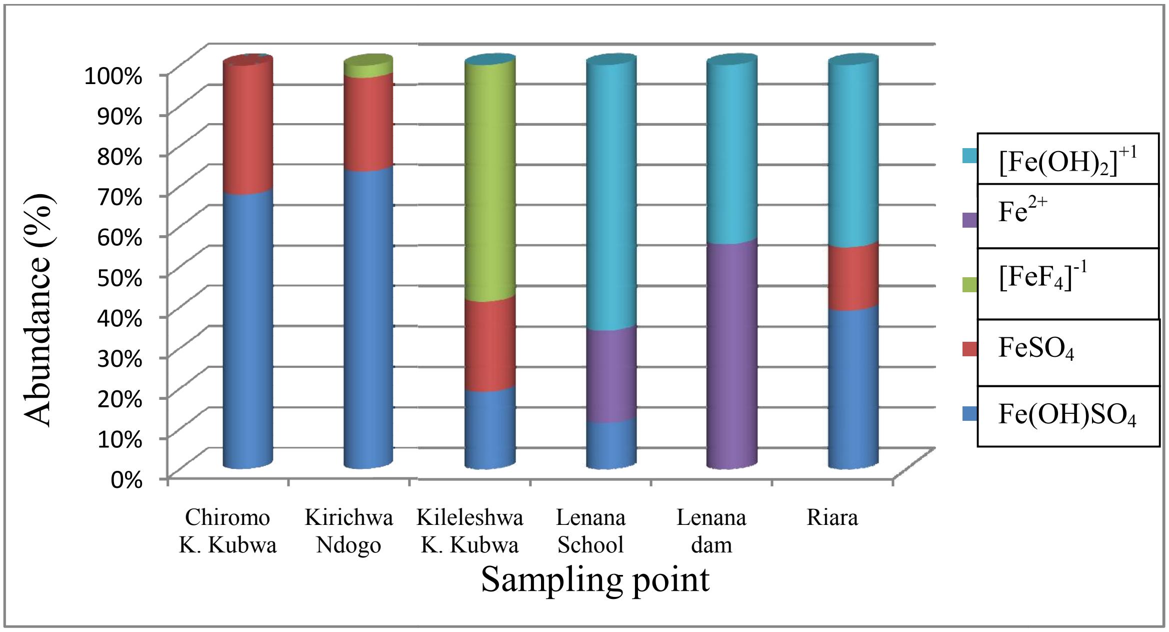

Figure 27: Percentage abundance of major iron species obtained during the dry season.

4.4.6 Manganese

Manganese was only found in oxidation state II. This is the most soluble, and hence more bioavailable form of manganese compared to other forms [Heal, 2001]. 72% of manganese formed compounds with fluoride and the rest were sulphates, free Mn^{2+} nitrites, hydroxides and chlorides in decreasing order (Tables 16 and 17). It is evident that manganese II dominates at pH 6.89-7.77 and that manganese -sulphate complexes are formed at pH above 7.59 while manganese fluoride complexes are formed mostly at pH less than 7.6. The $[MnF_6]^{-4}$ ion dominates in Kirichwa Ndogo during the wet season, most probably because of the low manganese concentration (Table 10) and a relatively high fluoride concentration at that sampling point (Table 6). The other fluoride species at that sampling point are $[MnF_4]^{-2}$ and $[MnF_5]^{-3}$ and are of lower abundance. This is also observed in Lenana School where the manganese concentration is quite low (Table 10) and fluoride concentration is relatively high (Table 6). Manganese sulphate species dominates in Kileleshwa Kirichwa Kubwa and Riara during the wet season mainly because of the high sulphate ion concentration in these points (Table 5). In Chiromo Kirichwa Kubwa, the sulphate species does not dominate despite the relatively high concentration, most probably due to the higher fluoride concentration (Table 6). During the dry season, the free Mn^{2+} was observed at Riara (0.4018 mg/L), Lenana School (1.166 mg/L) and Lenana dam (0.7793 mg/L) which is similar to the results observed with iron speciation when the lower anion concentration triggered the presence of $Fe^{2+.}$ This indicates that when removing pollutants from aqueous systems, it is important to maintain balance and not to concentrate on removal of some pollutants and leave others since the environment and therefore speciation of the ions changes which may enhance the toxicity. The free ion is usually more toxic than an ion which is combined with other species. Differences in speciation between Chiromo Kirichwa Kubwa and Kileleshwa Kirichwa Kubwa despite having the same concentration of sulphate during the dry season, is due to the great difference in manganese concentration (Table 10) between the two points which confirms the earlier statement that speciation is largely dependent on the total concentration of the species present. As noted in the iron speciation, the manganese chloride species observed in the speciation of chloride (Figure 23) is not visible here most probably due to the high reactivity of the fluoride ion over the chloride ion. The concentrations of $[MnF_3]^{-1}$, $[MnF_4]^{-2}$ and $[MnF_5]^{-3}$ were high during the wet season as compared to the dry season except at Kirichwa Ndogo (Figures 28 and 29) despite of low concentration of manganese during the wet season as compared to the dry season. The concentration of MnF_2, on the other hand was higher during the dry season as compared to the wet season in all the sampling points except at Kileleshwa Kirichwa Kubwa.

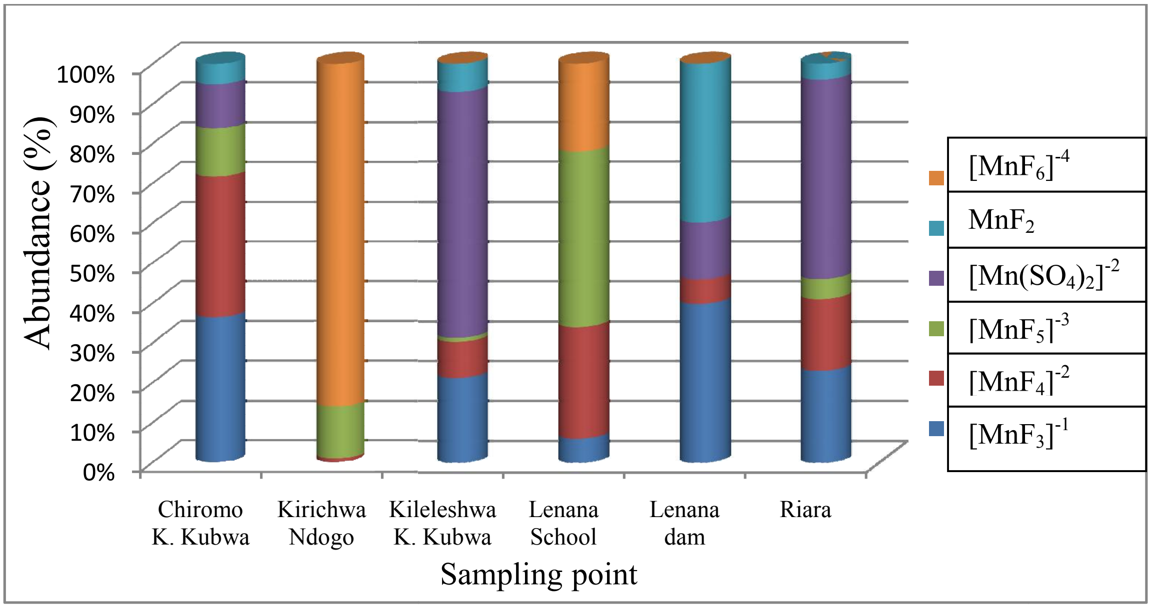

Figure 28: Percentage abundance of major manganese species obtained during the wet season.

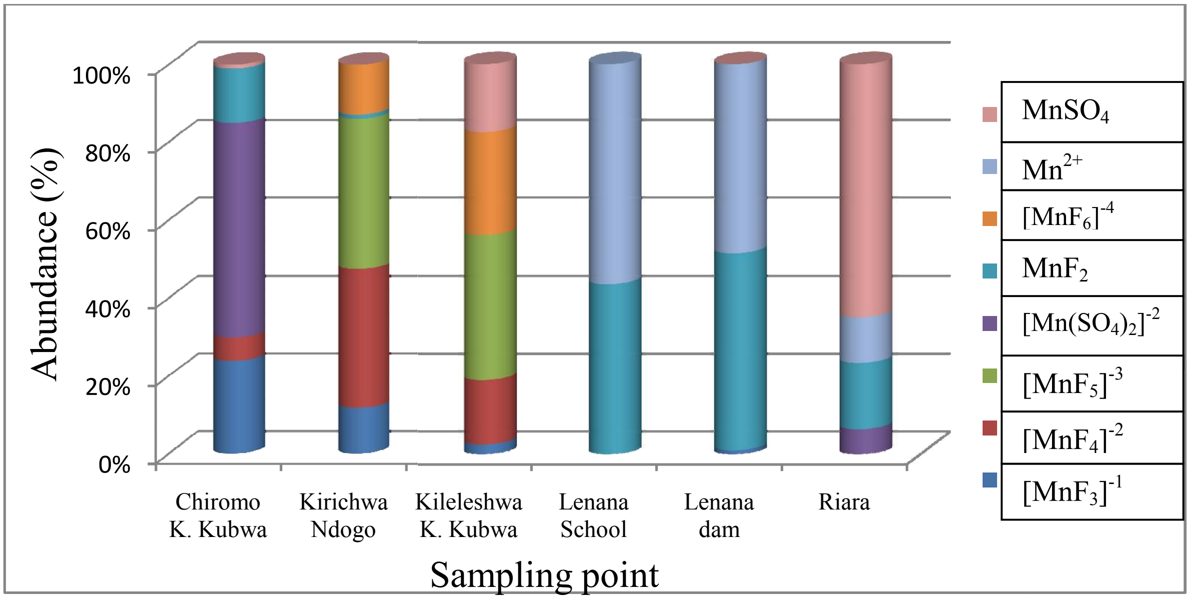

Figure 29: Percentage abundance of major manganese species obtained during the dry season.

4.4.7 Copper

Copper was found mainly (> 98%) in oxidation state II and the chemical forms of were mainly Cu^{2+}, sulphate, and hydroxide complexes. It is evident that at pH range of 6.89-7.77 copper predominates at oxidation state II and that it is mostly bound to sulphates since in this study, 99% of copper was in form of sulphates (Figures 30 and 31) and others (hydroxides, nitrites, and chlorides) were present only in small quantities. The concentrations of $[Cu(SO_4)_3]^{-4}$ and $[Cu(SO_4)_2]^{-2}$ were higher during the wet season as compared to the dry season. This might be because the concentrations of both copper (Table 11) and sulphates (Table 5) were high during the wet season. Cu^{2+} which is the second most toxic form of copper [Jones and Bolam, 2007] was present at Lenana School during the wet season (Figure 31).

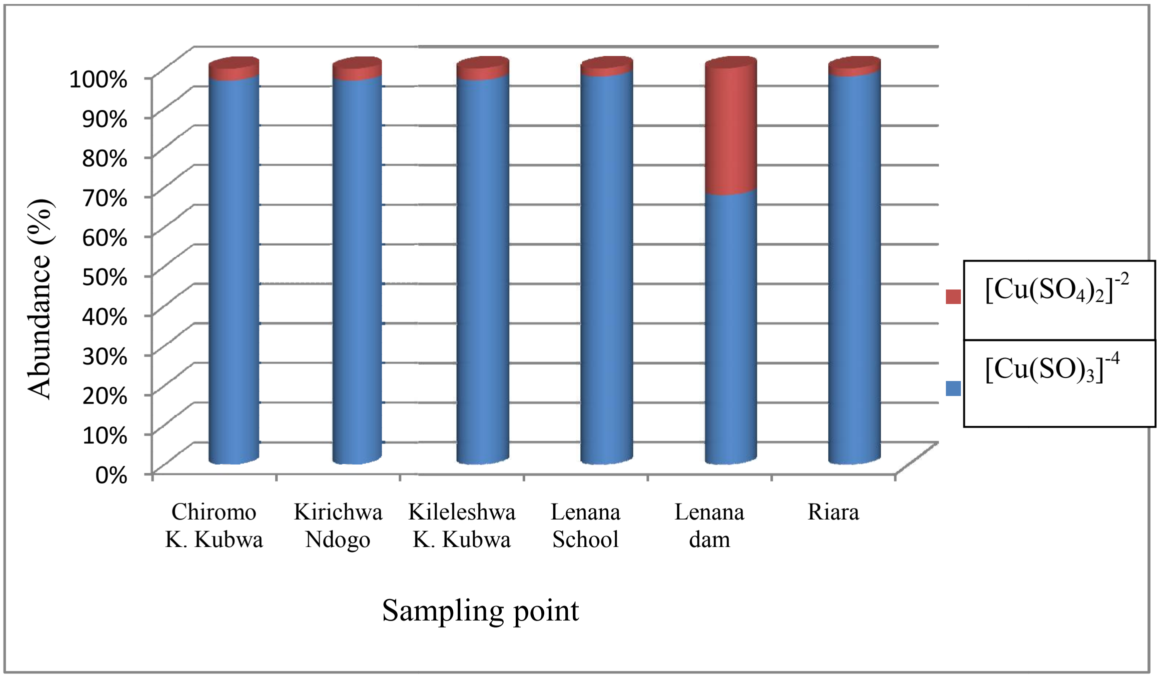

Figure 30: Percentage abundance of major copper species obtained during the wet season.

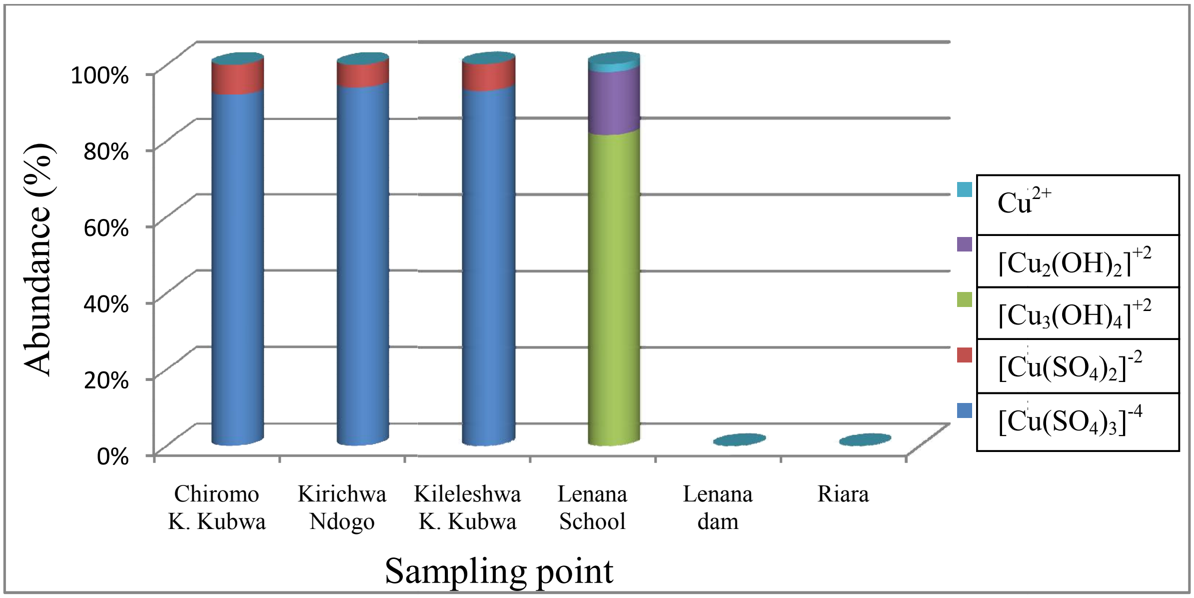

Figure 31: Percentage abundance of major copper species obtained during the dry season.

The difference in speciation at Lenana dam during the wet season was mainly due to the lower sulphate concentration at that sampling point (Table 5) and therefore $[Cu(SO_4)_2]^{-2}$ was observed unlike the other sampling points where the dominant chemical form was $[Cu(SO_4)_3]^{-4}$. During the dry season, the speciation at Lenana School was remarkably different from that in other sampling points due to the lower concentration of anions (sulphates, fluorides, nitrites and chlorides) at that sampling point. Therefore, the main species are the hydroxides and free Cu^{2+}. It is interesting that the fluoride and chloride ions did not combine with copper, as with manganese and iron. This is most probably due to lower reactivity of copper compared to iron and manganese.

4.4.8 Zinc

Zinc was divalent and its major chemical forms were sulphate complexes (Figure 32); this was attributed to high concentrations of sulphate compared to all the other anions. The predominance of $[Zn(SO_4)_4]^{-6}$ was as a result of relatively higher concentration of sulphate and lower concentration of zinc. $[Zn(SO_4)_2]^{-2}$ dominate at Lenana dam during the wet season, most probably due to low concentration of sulphate at this sampling point which was also coupled to other metals (copper, lead and iron) that were present. The percentage abundance of zinc species during the dry season were $[Zn(SO_4)_4]^{-6}$ (90%), $[Zn(SO_4)_2]^{-2}$ (6%) and $[Zn(SO_4)_3]^{-4}$ (3%).

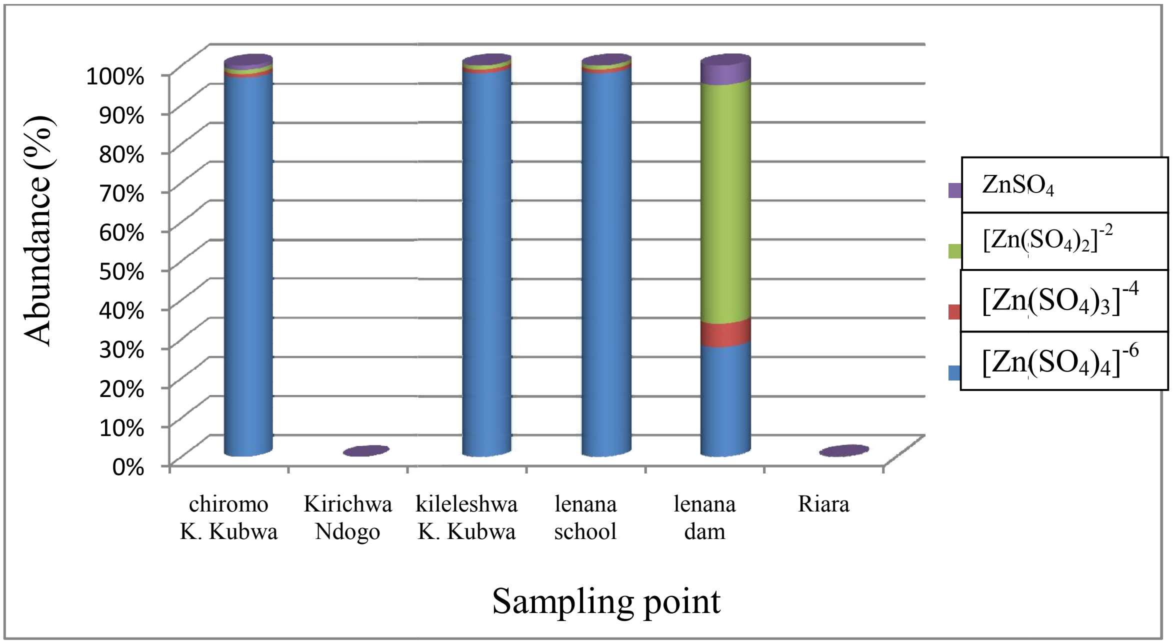

Figure 32: Percentage abundance of major zinc species obtained during the wet season.

4.4.9 Lead

Like zinc, lead was divalent and lead sulphate complexes were the dominant species; this was attributed to high concentration of sulphate compared to other anions (fluorides, chlorides and nitrites). The dominant chemical form of lead was found to be $[Pb(SO_4)_4]^{-6}$ (Figure 33). This is most probably due to relatively higher concentration of sulphate (Table 5) and lower lead concentration (Table 13). Unlike other sampling points, $[Pb(SO_4)_3]^{-4}$ was present in Lenana dam during the wet season in significant quantities; this was attributed to low concentration of sulphate at that sampling point compared to the other sampling points. Like the concentrations of lead and sulphate, the concentration of $[Pb(SO_4)_4]^{-6}$ was high during the wet season as compared to the dry season. During the dry season, the percentage abundance for $[Pb(SO_4)_4]^{-6}$ was 96% and that of $[Pb(SO_3)_4]^{-4}$ was 4% in Chiromo Kirichwa Kubwa and Kileleshwa Kirichwa Kubwa.

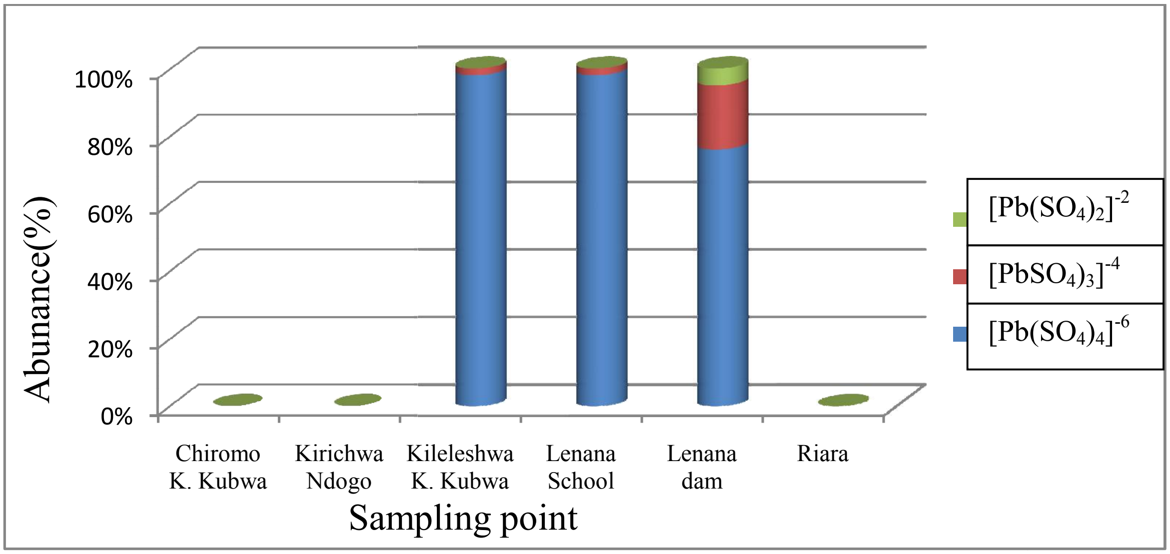

Figure 33: Percentage abundance of major lead species obtained during the wet season.

4.4.10 Chromium

Chromium was present mainly in oxidation state III, which is the predominant chromium form in surface waters [Swietlik, 1998]; this form is stable in nature and biological systems. The chemical forms were mainly hydroxides and hydroxide-sulphate complexes (Figure 34). $[Cr_4(OH)_6]^{+6}$ was the major chemical form of chromium. The presence of $Cr(OH)(SO_4)$ in Chiromo Kirichwa Kubwa was attributed to high concentration of sulphates at this sampling point (14 mg/L), unlike Lenana School (1.0 mg/L) and Lenana dam (0.0 mg/L) where the concentration of sulphate was low and hence absence of $Cr(OH)SO_4$. The contribution of chlorides, nitrites, and fluorides to chromium at pH 6.89-7.77 was insignificant.

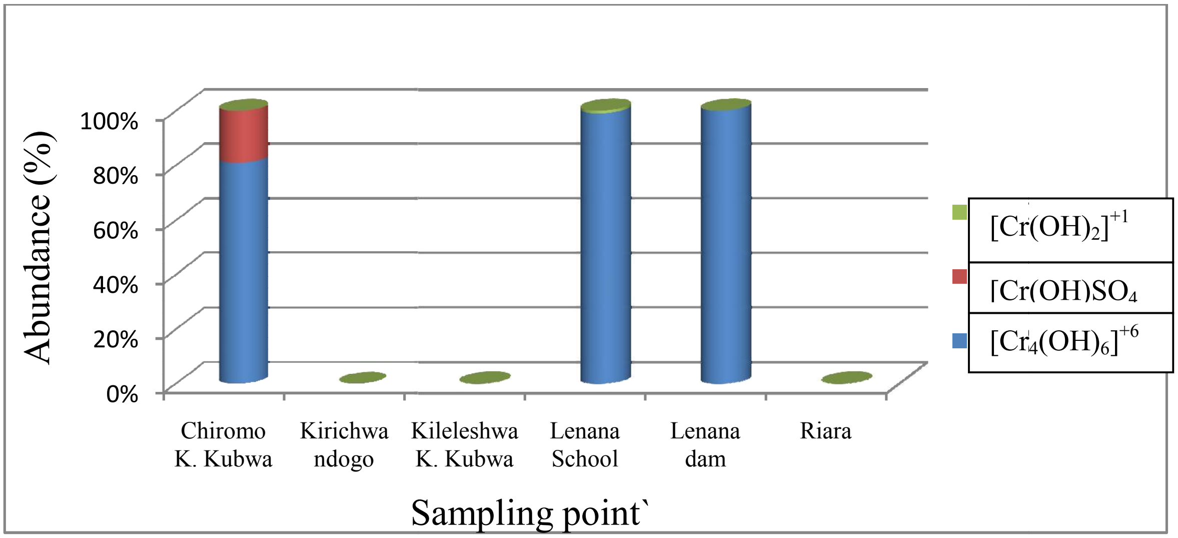

Figure 34: Percentage abundance of major chromium species obtained during the dry season.

CHAPTER FIVE

Conclusion and Recommendations

Conclusion

The study findings indicated that the pH range was 6.89-7.77 which was within the acceptable WHO, KEBS and EU limit for natural water. Temperature, EC, TDS, TSS, DO, BOD, COD, chloride, sulphate, phosphate, fluoride, nitrite, zinc, copper, iron, manganese, chromium and lead were observed to range from 18.3 to 25^{o}C, 348 to 881µS/cm, 176 to 438 mg/L, 131 to 414 mg/L, 8.10 to 24.29 mg/L,10.93 to 25.26 mg/L, 40 to 730 mg/L, 0.0142 to 0.8860 mg/L, 0 to 68 mg/L, 0.03 to 5.96 mg/L, 0.39 to 2.87 mg/L and 0.002 to 0.585 mg/L BDL to 0.0197 mg/L, BDL to 0.1799 mg/L, 0.0974 to 3.1438 mg/L, 0.0092 to 3.6843 mg/L, BDL to 0.0846 mg/L and BDL to 0.4415 mg/L respectively. The levels of TDS, DO, chloride, sulphate, nitrite, zinc and copper were below the KEBS limits for natural water in all the sampling points. The concentration of anions (Cl^-, F^-, SO_4^{2-}, and NO_2^-), heavy metals (zinc, copper and lead), TSS and electrical conductivity were high during the wet season compared to the dry season while that of BOD, COD, manganese, iron and chromium were high during the dry season as compared to the wet season. 69.8% of iron was in oxidation state III, the rest being of oxidation state II, and the dominant species was iron sulphate compounds. Fe^{2+} ion which is the most toxic form of iron was present at Lenana School (0.4582 mg/L) and Lenana dam (0.4699 mg/L) during the dry season. Manganese was only found in oxidation state II and that 72% of manganese formed complexes with fluoride. Mn^{2+} was obtained at Riara, Lenana School and Lenana dam during the dry season, with concentrations higher than the maximum recommended value for the total manganese in domestic water by KEBS. Copper was found mostly in oxidation state II and copper sulphate complexes were the dominant species. Cu^{2+} which is the second most toxic form of copper was present at Lenana School during the dry season. Zinc and lead were divalent and formed compounds mainly with sulphate. Chromium was present in oxidation state III with chromium hydroxide and chromium hydroxide-sulphate complexes being the only species formed. Despite the fact that some heavy metals were above their recommended values, most of them were bound to anions (sulphate, fluoride, chloride and nitrite) which make them less mobile and toxic than free ions. Waters from Riara, Lenana School and Lenana dam contained traces of free metal ions (Cu, Fe and Mn) during the dry season; this makes the water unfit for domestic and agricultural purposes since free metal ions are very mobile and toxic.

Recommendations

- JESS has proved to be a powerful tool for carrying out speciation of heavy metals in water and therefore authorities like NEMA should use this program to carry out speciation on other sampling points along Nairobi River since this study focused only on a small section which was mainly residential.
- Waters from Riara, Lenana School and Lenana dam during the dry season, contained traces of free metal ions (Fe^{2+}, Mn^{2+} and Cu^{2+}) therefore this makes the water unfit for domestic or even agricultural purposes.
- Sampling and speciation analysis should be conducted regularly in order to properly show how physicochemical parameters affect chemical speciation of heavy metals.
- Metal speciation should be incorporated into water quality guidelines since it gives more information regarding toxicity and mobility of heavy metals.
- Speciation of heavy metals in sediments should also be carried out because sediments act as a reservoir for heavy metals.

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Appendix

Table 14: Concentration distribution of iron species (mg/L) obtained during the wet season.

Species	Chiromo kirichwa kubwa	Kirichwa ndogo	Kileleshwa kirichwa kubwa	Lenana School	Lenana dam	Riara
$Fe(OH)SO_4$	0.2012	4.312×10^{-5}	0.3779	0.3268	0.8315	0.2120
$FeSO_4$	0.1150	2.577×10^{-5}	0.1836	0.5505	2.025	0.08566
$[Fe(OH)_2]^{+1}$	1.549×10^{-4}	—	3.472×10^{-4}	—	—	1.143×10^{-4}
$[Fe(SO_4)_2]^{-1}$	1.252×10^{-4}	—	—	5.365×10^{-4}	2.192×10^{-3}	1.71×10^{-4}
$Fe(OH)_3$	1.145×10^{-4}	—	2.879×10^{-4}	—	—	—
$[Fe(OH)_4]^{-1}$	—	—	2.503×10^{-4}	—	—	1.191×10^{-4}
$[FeF_4]^{-1}$	—	0.1522	—	0.1413	—	—
FeF_3	—	1.582×10^{-3}	—	0.01891	—	—
Fe^{2+}	—	—	—	—	5.448×10^{-3}	—
$[FeCl]^{+1}$	—	—	—	—	9.981×10^{-4}	—

Table 15: Concentration distribution of iron species (mg/L) obtained during the dry season.

Species	Chiromo kirichwa kubwa	Kirichwa ndogo	Kileleshwa kirichwa kubwa	Lenana School	Lenana dam	Riara
$Fe(OH)SO_4$	0.3355	0.2291	0.01749	0.2330	—	0.2533
$FeSO_4$	0.1593	0.07355	0.0286	—	—	0.1000
$[Fe(OH)_2]^{+1}$	8.035×10^{-4}	—	—	1.335	0.3773	0.2851
$Fe(OH)_3$	6.819×10^{-4}	—	—	0.5947	0.08818	0.2909
$[Fe(OH)_4]^{-1}$	6.089×10^{-4}	0.001083	—	0.2778	0.02161	0.3113
$[FeF_4]^{-1}$	—	0.008868	0.05391	—	—	—
FeF_3	—	0.001717	5.016×10^{-3}	—	—	—
$[FeF_2]^{+1}$	—	—	4.72×10^{-5}	—	—	—
Fe^{2+}	—	—	—	0.4582	0.4699	—
$[FeCl]^{+1}$	—	—	—	—	0.9631	—

Table 16: Concentration distribution of manganese species (mg/L) obtained during the wet season.

Species	Chiromo kirichwa kubwa	Kirichwa ndogo	Kileleshwa kirichwa kubwa	Lenana School	Lenana dam	Riara
$[MnF_3]^{-1}$	0.1596	4.672×10^{-6}	0.1644	0.02807	0.4516	0.2903
$[MnF_4]^{-2}$	0.1566	2.712×10^{-4}	0.07081	0.1266	0.06515	0.2226
$[MnF_5]^{-3}$	0.05326	5.461×10^{-3}	0.01058	0.1979	—	0.05918
$[Mn(SO_4)_2]^{-2}$	0.04844	—	0.4732	—	0.1675	0.6228
MnF_2	0.02351	1.163×10^{-8}	0.05514	9.005×10^{-4}	0.4525	0.05473
$[MnF_6]^{-4}$	—	0.03476	—	0.09782	—	—
$MnSO_4$	—	—	—	—	0.02475	—

Table 17: Concentration distribution of manganese species (mg/L) obtained during the dry season.

Species	Chiromo kirichwa kubwa	Kirichwa ndogo	Kileleshwa kirichwa kubwa	Lenana School	Lenana dam	Riara
$[Mn(SO_4)_2]^{-2}$	0.2849	—	—	—	—	0.2137
$[MnF_3]^{-1}$	0.1244	0.0182	2.836×10^{-4}	—	0.009454	—
MnF_2	0.07213	8.443×10^{-4}	6.324×10^{-6}	0.8905	0.7704	0.5773
$[MnF_4]^{-2}$	0.03102	0.05671	—	—	—	—
$MnSO_4$	7.457×10^{-3}	—	—	0.544	—	2.187
$[MnF_5]^{-3}$	—	0.06127	4.33×10^{-3}	—	—	—
$[MnF_6]^{-4}$	—	0.02093	2.938×10^{-3}	—	—	—
$[MnF_4]^{-2}$	—	—	1.839×10^{-3}	—	—	—
Mn^{2+}	—	—	—	1.166	0.7793	0.4018
$[MnNO_2]^{+1}$	—	—	—	—	—	0.2283
$[Mn_2(OH)_3]^{+1}$	—	—	—	0.03080	0.001790	—
$[MnCl]^{+1}$	—	—	—	0.009628	0.01615	—

Table 18: Concentration distribution of copper species (mg/L) obtained during the wet season.

Species	Chiromo kirichwa kubwa	Kirichwa ndogo	Kileleshwa kirichwa kubwa	Lenana School	Lenana dam	Riara
$[Cu(SO_4)_3]^{-4}$	0.1748	0.1486	0.1414	0.1367	0.08842	0.1385
$[Cu(SO_4)_2]^{-2}$	5.070×10^{-3}	0.004021	4.677×10^{-3}	4.425×10^{-3}	0.04116	0.002188
$CuSO_4$	2.813×10^{-5}	2.081×10^{-5}	2.834×10^{-5}	2.738×10^{-5}	0.003665	6.612×10^{-6}
$[CuCl_2]^{-1}$	3.518×10^{-6}	—	—	1.488×10^{-7}	—	—
$[Cu(NO_2)_3]^{-1}$	2.706×10^{-6}	—	2.994×10^{-6}	—	9.173×10^{-4}	4.035×10^{-7}
$[Cu(NO_2)_4]^{-2}$	—	—	1.314×10^{-6}	—	—	1.874×10^{-7}
$CuCl$	—	—	—	1.952×10^{-8}	—	—
$Cu(NO_2)_2$	—	—	—	—	2.942×10^{-4}	—
$[CuCl_2]^{-1}$	—	8.087×10^{-7}	—	—	—	—
$[CuCl_3]^{-2}$	—	6.768×10^{-8}	—	—	—	—

Table 19: Concentration distribution of copper species (mg/L) obtained during the dry season.

Species	Chiromo kirichwa kubwa	Kirichwa ndogo	Kileleshwa kirichwa kubwa	Lenana School	Lenana dam	Riara
$[Cu(SO_4)_3]^{-4}$	0.03682	9.368×10^{-3}	0.004641	—	—	—
$[Cu(SO_4)_2]^{-2}$	0.003036	6.238×10^{-4}	3.534×10^{-4}	—	—	—
$CuSO_4$	4.788×10^{-5}	7.943×10^{-6}	5.148×10^{-6}	1.732×10^{-4}	—	—
$[CuNO_2]^{+1}$	2.179×10^{-7}	1.331×10^{-8}	—	—	—	—
$[Cu(NO_2)_3]^{-1}$	1.488×10^{-7}	—	3.926×10^{-7}	—	—	—
$[Cu(NO_2)_4]^{-2}$	—	—	4.410×10^{-7}	—	—	—
$[Cu_3(OH)_4]^{+2}$	—	—	—	0.01188	—	—
$[Cu_2(OH)_2]^{+2}$	—	—	—	2.441×10^{-3}	—	—
Cu^{2+}	—	—	—	2.999×10^{-4}	—	—
$[Cu(OH)]^{+1}$	—	3.787×10^{-9}	—	1.655×10^{-4}	—	—

Table 20: Concentration distribution of zinc species (mg/L) obtained during the wet season.

Species	Chiromo kirichwa kubwa	Kirichwa ndogo	Kileleshwa kirichwa kubwa	Lenana School	Lenana dam	Riara
$[Zn(SO_4)_4]^{-6}$	0.01927	—	0.01745	0.004115	0.001789	—
$[Zn(SO_4)_3]^{-4}$	2.582×10^{-4}	—	2.609×10^{-4}	6.149×10^{-5}	3.48×10^{-4}	—
$[Zn(SO_4)_2]^{-2}$	1.632×10^{-4}	—	1.84×10^{-4}	4.334×10^{-5}	3.902×10^{-3}	—
$[ZnCl(SO_4)_2]^{-3}$	3.732×10^{-6}	—	2.496×10^{-6}	2.065×10^{-7}	—	—
$ZnSO_4$	7.601×10^{-7}	—	9.566×10^{-7}	2.252×10^{-7}	2.917×10^{-4}	—
$[Zn(Cl)SO_4]^{-1}$	—	—	—	—	1.974×10^{-5}	—

Table 21: Concentration distribution of zinc species (mg/L) obtained during the dry season.

Species	Chiromo kirichwa kubwa	Kirichwa ndogo	Kileleshwa kirichwa kubwa	Lenana School	Lenana dam	Riara
$[Zn(SO_4)_4]^{-6}$	0.01733	—	—	—	—	—
$[Zn(SO_4)_2]^{-2}$	1.186×10^{-3}	—	—	—	—	—
$[Zn(SO_4)_3]^{-4}$	6.603×10^{-4}	—	—	—	—	—
$ZnSO_4$	1.571×10^{-5}	—	—	—	—	—
$[ZnCl(SO_4)_2]^{-3}$	2.174×10^{-6}	—	—	—	—	—

Table 22: Concentration distribution of lead species (mg/L) obtained during the wet season.

Species	Chiromo kirichwa kubwa	Kirichwa ndogo	Kileleshwa kirichwa kubwa	Lenana School	Lenana dam	Riara
$[Pb(SO_4)_4]^{-6}$	—	—	0.4338	0.3564	0.03576	—
$[Pb(SO_4)_3]^{-4}$	—	—	0.00757	6.216×10^{-3}	8.974×10^{-3}	—
$[Pb(SO_4)_2]^{-2}$	—	—	1.457×10^{-4}	1.196×10^{-4}	2.484×10^{-4}	—
$PbSO_4$	—	—	2.202×10^{-7}	1.806×10^{-7}	5.40×10^{-5}	—
$Pb(NO_2)_2$	—	—	2.276×10^{-8}	—	2.412×10^{-5}	—
$[PbF_4]^{-2}$	—	—	—	1.493×10^{-9}	—	—

Table 23: Concentration distribution of lead species (mg/L) obtained during the dry season.

Species	Chiromo kirichwa kubwa	Kirichwa ndogo	Kileleshwa kirichwa kubwa	Lenana School	Lenana dam	Riara
$[Pb(SO_4)_4]^{-6}$	0.01720	—	0.06031	—	—	—
$[Pb(SO_4)_3]^{-4}$	7.645×10^{-4}	—	2.476×10^{-3}	—	—	—
$[Pb(SO_4)_2]^{-2}$	3.748×10^{-5}	—	1.121×10^{-4}	—	—	—
$PbSO_4$	1.443×10^{-7}	—	3.986×10^{-7}	—	—	—
$Pb(NO_2)_2$	1.941×10^{-9}	—	4.410×10^{-8}	—	—	—

Table 24: Concentration distribution of chromium species (mg/L) obtained during the dry season.

Species	Chiromo kirichwa kubwa	Kirichwa ndogo	Kileleshwa kirichwa kubwa	Lenana School	Lenana dam	Riara
$[Cr_4(OH)_6]^{+6}$	0.06828	–	–	0.03261	0.07488	–
$Cr(OH)(SO_4)$	0.01574	–	–	–	–	–
$[Cr(OH)_2]^{+1}$	3.006×10^{-4}	–	–	1.810×10^{-4}	0.0001614	–
$[Cr_2(OH)_3]^{+3}$	1.221×10^{-4}	–	–	8.438×10^{-5}	0.0001279	–
$Cr(OH)_3$	–	–	–	1.069×10^{-5}	–	–
$[Cr_3(OH)_4]^{+5}$	–	–	–	7.944×10^{-6}	0.00002046	–
$[Cr(OH)]^{+2}$	–	–	–	–	0.000006282	–