Assessment of the impact of effluents discharge from Murang'a town and its environs on the water quality of river Mathioya, Murang'a County, Kenya

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DECLARATION

I do hereby declare that this thesis is my original work and has not been submitted in any other university for the award of a Degree

Signature…………………. Date………………………..

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Declaration by Supervisors:

This research thesis has been submitted for examination with our approval as university supervisors.

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DEDICATION

This work is dedicated to my family.

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LIST OF ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectroscopy
APHA	American Public Health Association
BOD	Biological Oxygen Demand
CAN	Calcium Ammonium Nitrate
COD	Chemical Oxygen Demand
CDTA	1,2 Cyclohexylene Dinitrilo Tetra acetic Acid
DAP	Di-Ammonium Phosphate
DO	Dissolved Oxygen
EC	Electrical Conductivity
ISE	Ion selective Electrode
LOD	Limit of detection
MPN	Most Probable Number
NEMA	National Environmental Management Agency of Kenya
NPK	Nitrogen Phosphorous and Potassium
pH	$-\log_{10}(H^+)$
TDS	Total Dissolved Solids
TISAB	Total Ionic Strength Adjustment Buffer
TSS	Total Suspended Solids
UNEP	United States Environmental Programme
UNESCO	United Nations Educational, Scientific and Cultural Organization
USEPA	United States Environmental Protection Agency
UV-VIS	Ultraviolet-visible

WHO	World Health Organization

ABSTRACT

Chemical fertilizers, leaching through the soil from agricultural activities, sewerage effluents and runoff from residential areas reaching water resources cause serious pollution. The purpose of this study was to determine the impact of effluent discharges on water quality of River Mathioya in Murang'a County, Kenya. Samples were collected upstream and downstream of Murang'a town along the river. The pH, Dissolved Oxygen, Electrical Conductivity, Total Dissolved Solid, Total Suspended Solids and Temperature were determined using the respective meters. Heavy metals were determined using Flame Atomic Absorption Spectrometry while Sodium and Potassium were determined using Flame Emission Photometry. Nitrates and Phosphates were determined using UV/Visible Spectrophotometry. Ion Selective Electrode was used to determine Fluoride levels.

The mean values of water temperature, TSS, TDS, DO, pH, EC, phosphates, nitrates and fluorides were found to be 22.44± 0.23^{o} C, 48.33± 0.59 mg/l, 5.74± 0.18 mg/l, 5.74± 0.05 mg/l, 7.34± 0.05 70.26± 0.89 µs/cm, 0.68± 0.04 mg/l, 10.84± 0.38 mg/l and 0.79± 0.01 mg/l respectively. The mean values of Fe, Mn, Zn, Cu, Pb, Cr, K and Na were found to be 1.01± 0.05, 1.50± 0.11, 0.07± 0.01, 0.03± 0.01, LOD, 0.03± 0.01, 9.51± 0.62 and 94.58± 0.44 mg/l respectively. The data was analyzed using Student-Newman-Keuls test. The study showed that there was small amounts of heavy metals in the water samples, though the levels were below WHO maximum permissible levels for Zn, Cr, Pb, and Cu. The levels of iron and manganese were higher than the recommended level of 0.5 mg/l and 0.04 mg/l respectively. The concentrations of the physicochemical parameters, nitrates and phosphates were found to be within the WHO limits for domestic water. It was recommended that close monitoring, proper use and disposal of agrochemicals, proper planning of vehicle repair and maintenance garages and proper location of car washing areas should be done.

CHAPTER ONE

INTRODUCTION AND LITERATURE REVIEW

1.1 Background of the study

Effect of effluents into rivers is of great economic, environmental and health concern. Chemical fertilizers are used extensively in modern agriculture, in order to improve yield and productivity of agricultural products. However, nutrient leaching from agricultural soil into river water resources poses a major environmental and public health concern. Sewerage effluents and runoff from residential areas reach the rivers causing serious water pollution (Asit & Cecilia, 2011).

Water quality is measured from chemical, physical and biological characteristics of water. It is a measure of the conditions of the water relative to the requirements of one or more biotic species and/or any human need or purpose. It is most frequently used for reference to a set of standards against which compliance can be assessed. Water quality depends on local geology and ecosystem, as well as human uses, such as sewage dispersion, industrial pollution, and use of water bodies as heat sinks (Asit & Cecilia, 2011). Water is a scarce and valuable resource and it is highly essential for the survival of mankind but, man-made activities are changing the morphology of the area of the river regimes and causing water pollution **(**Simpi et al., 2011).

Water pollution is the contamination of water bodies (e.g. lakes, river, oceans, aquifers and groundwater) by pollutants being discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds. Water pollution affects both the fauna and the flora living in these bodies of water. In almost all cases the effect is damaging not only to individual species and populations, but also to the natural biological communities (Azizullah, Khattak, Richer, & Hader, 2011).

The WHO states that one sixth of the World's population i.e. approximately 1.1 billion people, do not have access to safe water and 2.4 billion lack basic sanitation (European Public Health Alliance, 2009). Some water pollution effects are recognized immediately, whereas others not show up for months or years. In fact, the effects of water pollution are said to be the leading causes of death for humans across the globe. Moreover, water pollution affects our oceans, lakes, rivers, and drinking water, making it a widespread and global concern. The untreated industrial and municipal wastes have created multiple environmental hazards for mankind and jeopardizes irrigation, drinking and sustenance of aquatic life. The drainage water contains heavy metals in addition to biological contaminants (Ashraf, Maah, Yusoff, & Mehmood, 2010).

The indiscriminate and large scale deforestation and over-grazing in the watershed areas of river basins have caused soil erosion resulting in considerable silting of dams and shrinkage of river flows. This leads to the flooding of the rivers at the time of excessive rains (Dhirendra, Alok, & Namita, 2009*)*. The main threat to human health from heavy metals is associated with exposure to lead, cadmium, mercury and arsenic. Early application of lead includes building materials, pigments for glazing ceramics and pipes for transporting water **(**Sekabira et al., 2010).

Although adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues and is even increasing in some areas. For example, mercury is still used in gold mining in Latin America while arsenic is still common in wood preservatives **(**Aprile & Bouvy, 2008).

Emissions of heavy metals to the environment occur via a wide range of processes and pathways including the air (e.g. during combustion, extraction and processing), to the surface waters (via run off and leakages from storage and transport) and to the soil, (and hence into ground waters and crops) **(**Mohiuddin et al., 2010). Heavy metals are most persistent pollutants found in lake, reservoir and river sediments. Because of this, they act as useful markers of environmental change in the aqueous systems (Tukura, Kagbu, & Gimba, 2002). Heavy metals occur in water in the dissolved phase and are bound to suspended particulate matter, including phytoplankton. The total concentration in the water column and its distribution over the suspended matter and dissolved phase is governed by parameters such as physical mixing, re-suspension, re-dissolution from bottom sediments and sedimentation of suspended particles. Through precipitation of their compounds or by ion exchange into soils and mud, heavy metal pollutants can localize and lay dormant and later have severe effects on the environment **(**Muwanga & Barifaijo, 2006).

Fertilizers through leaching from farming areas has caused water pollution. The use of fertilizers has increased worldwide, especially in the developing countries. The application of nitrogen, ammonia, and potash fertilizers has increased threefold from 1990-2000 and these rates are expected to increase (Keramat, 2008). Small amounts of nutrients are essential for metabolism and growth of all aquatic organisms (Keramat, 2008). DAP, CAN and NPK fertilizers are commonly applied in Murang'a County. These fertilizer through run-off waters can find their way into River Mathioya.

1.2 Water Quality Parameters

1.2.1 Physico-Chemical Parameters

1. 2.1.1 pH

The pH is a measure of the acid balance of a solution and is defined as the negative of the logarithm to the base 10 of the hydrogen ion concentration (WHO, UNESCO & UNEP, 1996). Natural waters usually have pH values in the range of 6- 8.3. Most natural waters are slightly basic due to the presence of bicarbonates and carbonates of the alkali and alkaline earth metals (Nighojkar & Dohare, 2014). Drinking water with elevated pH, can cause skin; eye and mucous membrane irritation while that with pH values below 4 cause irritation due to the corrosive effects of low pH levels (WHO, UNESCO & UNEP, 1996). Aquatic wildlife also suffers from the effects of pH extremes for example fish die-off occurs when pH levels dip below 4.5 or rise above 10 (Himangshu, Amrita, & Ashis, 2012).

1.2.1.2 Electrical Conductivity

Electrical Conductivity (EC) is the numerical expression of an aqueous solution to carry electrical current and is a useful indicator of the mineralization in a water sample (Jain et al., 2005). Electrical conductivity is the capacity of water to conduct current, and is caused by the presence of salt, acids and bases i.e. electrolytes. Electrical conductivity is a function of total dissolved solids (TDS), which determines the quality of water. Conductivity itself is not a human or aquatic health concern, but because it is easily measured, it can serve as an indicator of other water quality problems (Nighojkar & Dohare, 2014). Waters with high TDS are unpalatable and potentially unhealthy. Discharge of wastewater with a high TDS level would have adverse impact on aquatic life, water wound be unfit for drinking and other domestic purposes, affect crop yield if used for irrigation, and exacerbate corrosion in water networks (Goel, 2009 & Pandey, Shubhashish, & Pandey, 2010).

1.2.1.3 Total dissolved solids

Total dissolved solids (TDS) are a measure of dissolved matter (salts, organic matter, and minerals) in water. Inorganic constituents comprise most of the total concentration of TDS. TDS can be naturally present in water or can be due to the result of mining, oil and gas drilling or some industrial or municipal waste. TDS can be toxic to aquatic life through increases in salinity or changes in the composition of the water. Most aquatic ecosystems involving mixed fish fauna can tolerate TDS levels of 1000 mg/l (Himangshu et al., 2012).

1.2.1.4 Total Suspended Solids

Total suspended solids (TSS) content of water depends on the amount of suspended particles, soil and silt. It is directly related to turbidity of water. Disposal of sewage and industrial effluents contribute to suspended matter in rivers (Himangshu et al., 2012). Organic particles from decomposing materials can also contribute to the TSS concentration. As algae, plants and animals decay, the decomposition process allows small organic particles to break away and enter the water column as suspended solids. Even chemical precipitates are considered a form of suspended solids (Keramat, 2008).

1.2.1.5 Dissolved Oxygen

Dissolved oxygen (DO) in water is essential for aquatic life. Deficiency of dissolved oxygen gives bad odor to water due to anaerobic decomposition of organic waste. It is essential for the life of fish and other aquatic organisms. Dissolved oxygen is an indicator of corrosiveness of water, photosynthetic activities, and “life of the water body.” The distribution of dissolved oxygen depends upon depth, turbulence and mixing, temperature, light, sludge deposits, microbial action, respiration of oxygen consuming species, and photosynthetic activity (oxygen producers) of phytoplankton. Wind currents and turbulence tend to increase the amount of dissolved oxygen in water. Oxygen levels in flowing water increase with disturbance caused by the rocks, fallen trees and waterfalls. Therefore a significant variation in dissolved oxygen concentration can be observed along a stream or a river (Chitmanat & Traichaiyaporn, 2010). Untreated sewage and rotting materials (such as garbage, leaves, sewage and wood) are often responsible for oxygen depletion in water bodies. This implies that wastes require a great amount of oxygen to decompose (Greenberg et al., 1985).

1.2.1.6 Fluoride

The amount of fluoride present naturally in non-fluoridated drinking water is highly variable, being dependent upon the individual geological environment from which the water is obtained. Many fluoride minerals are known, but of paramount commercial importance is fluorspar (CaF_2), which is roughly 49% fluoride by mass. The soft, colorful mineral is found worldwide. Seawater fluoride levels are usually in the range of 0.86 to 1.4 mg/L, and average 1.1 mg/L. Fluoride is the most bioavailable form of fluorine (Chan et al., 2013). Fluoride ion in low doses in the mouth reduces tooth decay. For this reason, it is used in toothpaste and water fluoridation. The main uses of fluoride, in terms of volume, are in the production of cryolite, $Na_3AlF_{6,}$ which is used in aluminium smelting. Fluorite is also used on a large scale to separate slag in steel-making. Fluoride-containing compounds, such as sodium fluoride or sodium monofluorophosphate are used in topical and systemic fluoride therapy for preventing dental fluorosis. Originally, sodium fluoride was used to fluoridate water. Hexafluorosilicic acid (H_2SiF_6) and its salt sodium hexafluorosilicate (Na_2SiF_6) are more commonly used additives, especially in the United States. The fluoridation of water is known to prevent tooth decay and is considered by the U.S. Centers for Disease Control and Prevention as "one of 10 great public health achievements of the 20th century" (McDonagh et al., 2000). Adequate fluoride ingestion is helpful to prevent fluorosis, but over ingestion induces dental and skeletal fluorosis, which may result in malfunction of the bones and joint system. The severity depends upon the amounts ingested and the duration on intake of fluoride (Institute of Medicine, 2007& WHO, 2002). Dental fluorosis is a condition where excessive fluoride can cause yellowing of teeth, white spots and pitting or mottling of enamel. Skeletal fluorosis is a bone disease exclusively caused by excessive consumption of fluoride (Griffin et al., 2007).

1.2.2 Macro-nutrients

1.2.2.1 Potassium

Potassium plays a vital role in the physiological and bio-chemical functions of plants, animals and other types of species (Mahananda et al., 2005). In plants, potassium enhances disease resistance by strengthening stalks and stems. It activates specific enzyme systems, and contributes to a thicker cuticle which guards against disease and water loss (Greenberg et al., 1985).

1.2.2.2 Phosphates

High quantities of phosphate in water can contribute to eutrophication problems in rivers, ponds and lakes **(**Akan et al., 2008).The rapid growth of algae and phytoplankton can decrease the amount of dissolved oxygen in a body of water. Most human and animal waste contains some phosphate material. As a result, phosphate materials enter water sources through the use of fertilizers, sewage dumping and garbage disposal in landfills (Greenberg et al., 1985). Excess phosphate in water promotes an algal bloom. Algae reproduce and die rapidly, and the decomposition of algae depletes dissolved oxygen in the water. Thus, the aquatic organism population can be seriously jeopardized and minimized **(**Toufeek & Korium, 2008).

1.2.2.3 Nitrates

Nitrate is the most highly oxidized form of nitrogen compound commonly present in natural waters. It is a product of aerobic decomposition of organic nitrogenous matter (Camargo, Alonso, & Salamanca, 2005). Nitrates are found in many different minerals. Nitrate forming bacteria convert nitrites to nitrates under aerobic conditions. Nitrates are often in water effluents from areas of relatively high population density and effluents from a variety of industries. Nitrate levels in water promote plant growth and appear to trigger algae blooms (Greenberg et al., 1985).

1.2.3 Heavy Metals in Water

A heavy metal is a member of loosely defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides and actinides. Heavy metals occur naturally in the ecosystem with large variation in concentration. In modern times, anthropogenic sources of heavy metal, have been introduced to the ecosystem (Duffus, 2002).

Through precipitation of their compounds or by ion exchange into soil, heavy metal pollutants can localize and lay dormant, which can have severe effects on the environment. Unlike organic pollutants, heavy metals do not decay and thus pose a different challenge for remediation. Plants, mushrooms, or microorganisms are occasionally successfully used to remove some heavy metals such as mercury. Some heavy metals such mercury, cadmium, lead and chromium are dangerous to health or to the environment, while others may cause corrosion (Muhammad, Tasneem, & Muhammad, 2008).

1.2.3.1 Iron

Iron is the sixth most abundant element and the most common refractory element. It is formed as the final exothermic stage of stellar nucleosynthesis, by silicon fusion in massive stars, (McDonald et al.,).Metallic or native iron is rarely found on the surface of the earth because it tends to oxidize, but its oxides are pervasive and represent the primary ores. While it makes up about 5% of the earth's crust, both the earth's inner and outer core are believed to consist largely of an iron-nickel alloy constituting 35% of the mass of the earth as a whole. Iron is consequently the most abundant element on earth, but only the fourth most abundant element in the earth's crust. Most of the iron in the crust is found combined with oxygen as iron oxide minerals such as hematite (Fe_2O_3) and magnetite (Fe_3O_4) (Morgan & Anders, 2008).

Iron forms compounds mainly in the +2 and +3 oxidation states. Iron also occurs in higher oxidation states, an example being the purple potassium ferrate (K_2FeO_4) which contains iron in its +6 oxidation state. Iron (IV) is a common intermediate in many biochemical oxidation reactions. Numerous organometallic compounds contain formal oxidation states of +1, 0, −1, or even −2. The oxidation states and other bonding properties are often assessed using the technique of Mössbauer spectroscopy. There are also many mixed valence compounds such as magnetite and Prussian blue (Fe_4 (Fe [CN] $_6)_3$) that contain both iron (II) and iron (III) centers (Klingelhofer et al., 2007).

The iron compounds produced on the largest scale in industry are iron (II) sulfate ($FeSO_4 \cdot 7H_2O$) and iron (III) chloride ($FeCl_3$). The former is one of the most readily available sources of iron (II), but is less stable to aerial oxidation than Mohr's salt ($(NH_4)_2Fe\ (SO_4)_2 \cdot 6H_2O$). Iron (II) compounds tend to be oxidized to iron (III) compounds in the air. Unlike many other metals, iron does not form amalgams with mercury (Klingelhofer et al., 2007).

Iron chemical compounds have many uses, iron oxide mixed with aluminium powder can be ignited to create a thermite reaction used in welding and purifying ores. It forms binary compounds with the halogens and the chalcogens, among its organometallic compounds is ferrocene, the first sandwich compound discovered. It plays an important role in biology, forming complexes with molecular oxygen in hemoglobin and myoglobin; these two compounds are common oxygen transport proteins in vertebrates (Sandhu & McPherson, 2001). It is also the metal used at the active site of many important redox enzymes dealing with cellular respiration and oxidation and reduction in plants and animals. Iron is important to a healthy body, and deficiency in the body causes anemia. Iron in water can cause staining of laundry and porcelain. Silt and clay in suspension often contain significant amount of iron. In water, iron as ferrous and ferric ions may remain in solution; exist in a colloidal state, form organic and inorganic complexes or form coarse suspended particles, can enter water systems from natural deposits, industrial waste effluents, and acid mine drainage (Sandhu & McPherson, 2001).

High blood levels of free ferrous iron react with peroxides to produce free radicals, which are highly reactive and can damage DNA, proteins, lipids, and other cellular components. Thus, iron toxicity occurs when there is free iron in the cell, which generally occurs when iron levels exceed the capacity of transferrin to bind the iron. Damage to the cells of the gastrointestinal tract can also prevent them from regulating iron absorption leading to further increases in blood levels. Typically can damages cells in the heart, liver, which can cause significant adverse effects, including coma, metabolic acidosis, shock, liver failure, coagulopathy, adult respiratory distress syndrome, long-term organ damage, and even death. Humans experience iron toxicity above 20 milligrams of iron for every kilogram of mass, and 60 milligrams per kilogram is considered a lethal dose. Overconsumption of iron, often the result of children eating large quantities of ferrous sulfate tablets intended for adult consumption, is one of the most common toxicological causes of death in children under six. The Dietary Reference Intake, lists the tolerable upper intake level for adults as 45 mg/day. For children under fourteen years old is 40 mg/day (Tenenbein, 2006).

1.2.3.2 Manganese

Manganese makes up about 1000 ppm (0.1%) of the Earth's crust, making it the 12th most abundant element. Soil contains 7–9000 ppm of manganese with an average of 440 ppm. Seawater has only 10 ppm manganese and the atmosphere contains 0.01 µg/m^3 **(**Emsley 2001). Manganese occurs principally as pyrolusite (MnO_2). Methylcyclopentadienyl manganese tricarbonyl is used as an additive in unleaded gasoline to boost octane rating and reduce engine knocking. Manganese dioxide, is also used in the manufacture of oxygen and chlorine, and in drying black paints. Manganese is an important metal for human health, being absolutely necessary for development, metabolism, and the antioxidant system (Mccray, 1998). Nevertheless, excessive exposure or intake may lead to a condition known as manganism, a neurodegenerative disorder that causes dopaminergic neuronal death and parkinsonian- like symptoms. Exposure to manganese dusts and fumes should not exceed the ceiling value of 5 mg/m^3 even for short periods because of its toxicity level. Manganese poisoning has been linked to impaired motor skills and cognitive disorders. It functions as an antiknock agent by the action of the carbonyl groups. Fuels containing manganese tend to form manganese carbides, which damage exhaust valves (Elsner & Spangler, 2005).

1.2.3.3 Zinc

Zinc makes up about 75 ppm (0.0075%) of the earth's crust, making it the 24th most abundant element. Soil contains 5–770 ppm of zinc with an average of 64 ppm. (Ingalls, 2002). The element is normally found in association with other base metals such as copper and lead in ores. Zinc is a chalcophile, meaning the element has a low affinity for oxides and prefers to bond with sulfides. Sphalerite (ZnS), which is a form of zinc sulfide, is the most heavily mined zinc-containing ore because its concentrate contains about 60–62% zinc (Ingalls, 2002).

Zinc deficiency is usually due to insufficient dietary intake, but can be associated with absorption, chronic liver disease, chronic renal disease, sickle cell disease, diabetes and other chronic illnesses. Clinical outcomes include depressed growth, diarrhea, impotence and delayed sexual maturation, impaired appetite, altered cognition, impaired host defense properties, and defects in carbohydrate utilization (Prasad, 2003).

Although zinc is an essential requirement for good health, excess zinc can be harmful. Excessive absorption of zinc suppresses copper and iron absorption. The free zinc ion in solution is highly toxic to plants, invertebrates, and even fish. Zinc enters the water supply by deterioration of brass and galvanized iron and through waste pollution. Stomach acid contains hydrochloric acid, in which metallic zinc dissolves readily to give corrosive zinc chloride which can cause damage to the stomach lining. However, zinc is a beneficial element in human growth and is often added to food such as cereals (Dawn & Benjamin, 2003).

1.2.3.4 Copper

Copper is present in the earth's crust at a concentration of about 50 parts per million, where it occurs as native copper or in minerals such as the copper sulfides chalcopyrite and chalcocite, the copper carbonates azurite and malachite, and the copper (I) oxide mineral cuprite’s (Callatay & Francois, 2005). Although it can be found in pure form, copper is generally locked together with other minerals such as gold, lead, zinc and silver. Copper is a reddish metal that occurs naturally in rock, soil, water, sediment and air, its average concentration in the earth’s crust is about 50 µg/g. It is an essential element for all known living organisms including humans and other animals. In the human body, the adult daily requirement of copper is approximately 2.0 mg (Schmitz, 1986).

There are many industrial uses of copper. Due to its high ductility, malleability, thermal conductivity and resistance to corrosion. It is alloyed with nickel, Copper compounds are used in water supply systems to minimize biological growth (such as algae) in water reservoirs, lakes, ponds and distribution pipes, roofing and about 65% of copper that is produced is used for electrical applications. Measureable amount of copper may be introduced into drinking water by corrosion of copper containing alloys in the pipe fittings. Copper may occur in natural waters, waste waters and industrial waters as soluble salts and precipitated copper compounds (Callatay & Francois, 2005).

Large amounts of orally ingested copper become toxic. The exposure limit is 1 µg/g for man. Inhalation causes irritation of mucous membrane, nasal perforation, cough, dry throat, muscle ache, chills and metal fever. Skin contact can result in dermatitis. Diseases caused by high concentrations of copper include anaemia, chromatosis, cirrhosis, and yellow atrophy of the liver and tuberculosis. Copper in water is exceedingly toxic to aquatic fauna. For example, at levels as low as 0.0025 to 0.005 µg/g, copper is lethal to fish and other aquatic invertebrates. The USEPA 2009, guideline for Cu in seawater is 3.1µg/l and 108 µg/g in sediments (Rickard, 2000).

1.2.3.5 Lead

Metallic lead does occur in nature, but it is rare. Lead is usually found in ores with zinc, silver and (most abundantly) copper, and is extracted together with these metals. The main lead mineral is galena, other common varieties are Cerussite ($PbCO_3$) and anglesite ($PbSO_4$) **(**Nyangababo & Omutange, 2005). Lead is used as electrodes in the process of electrolysis, as shielding from radiation (e.g.; in X-ray rooms) and added to brass to reduce machine tool wear. Molten lead is used as coolant (e.g. for lead cooled fast reactors) and lead metal is used to make lead acid batteries (Dayan & Paine, 2001). Lead is a poison, and once taken into the human body it enters the blood from where it is redistributed to the soft tissue and the skeleton. The biological half-life of lead in human bone is estimated to be 10 years (UNEP, 1984). The clinical manifestations of lead poisoning include abdominal colic, anaemia, renal damage, neuropathy and rarely, encephalopathy. Toxic effects of lead have been reported on the human foetus, and this has prompted restrictions on employment of women in lead industries (UNEP, 1984). The symptoms of acute lead poisoning are headache, irritability, abdominal pain and various symptoms related to the nervous system. People who have been exposed to lead for a long time may suffer from memory deterioration and reduced ability to understand. Acute exposure of lead causes proximal renal tubular damage. Long term exposure may also give rise to kidney damage, (Nyangababo & Omutange, 2005).

1.2.3.6 Chromium

Chromium is the 22nd most abundant element in the earth's crust with an average concentration of 100 ppm. Chromium compounds are found in the environment due to erosion of chromium containing rocks and can be distributed by volcanic eruptions. The concentration ranges in soil are between 1 and 300 mg/kg; in sea water, 5 to 8 mg/litre and in rivers and lakes 0.026 mg/ litre to 5.2mg/litre. Chromium is mined as Chromite's ($FeCr_2O_4$) ore (Gonzalez & Flegal, 2005). Chromium is used for electroplating, as a protective and decorative coating on car parts, plumbing fixtures, furniture parts and many other items (usually applied by electroplating), in metal alloying, in chemical industry, refractory and foundry industries. Chromium (VI) salts are used for the preservation of wood; chromate-copper-arsenate is used in timber treatments to protect wood from decay, fungi and wood-attacking insects (termites and marine borers). Chromic acid is a powerful oxidizing agent and is a useful compound for cleaning laboratory glassware of any trace of organic compounds (Ilhan et al., 2004).

Several *in vitro* studies indicated that high concentrations of chromium (III) in the cell can lead to DNA damage. Chromium (III) is essential and assists in the regulation of blood sugar while chromium (VI) is known to be toxic. The acute toxicity of chromium (VI) is due to its strong oxidation properties. After it reaches the blood stream, it damages the kidneys, liver and blood cells through oxidation reactions. Hemolysis, renal and liver failure are the results of these damages. Aggressive dialysis can improve the situation (Dayan & Paine, 2001).

1.2.4 Review of Previous Studies on Water Quality

Physicochemical and bacteriological characteristics of water samples from Irigu River, Meru south, Kenya, were investigated by Ombaka & Gichumbi, 2012 and the results showed that the physico-chemical parameters analyzed were in compliance with the WHO, 2006 standards except pH, turbidity, phosphorus, iron, manganese, lead and aluminum. The values of Most Probable Number (MPN) of coli form organisms/ 100 ml and *E. coli* form/100 ml were above the recommended values by World Health Organization, 2006. The water from Irigu was found unsafe for domestic use and required purification. Therefore there was need for awareness programs to educate local villagers to safeguard the river (Ombaka & Gichumbi, 2012 and Ombaka & Kibara 2013).

A study was carried out on heavy metals in water and tilapia fish from Athi-Galana-Sabaki tributaries, Kenya, and the results showed that the concentrations of Pb, Mn, Cd and Cr in water, and Pb, Ni and Mn in fish gills were found to be higher than the WHO recommended limit thus posing immediate fears of bioaccumulation in man. Constant monitoring of heavy metals concentration in Athi River was recommended since the river serves as a source of drinking water, irrigation and fisheries for the local inhabitants **(**Muiruri & Nawiri, 2013).

A study on the effects of effluent discharge by Mumias Sugar Company on the pollution of river Nzoia in Kenya was carried out and the findings indicated that the measured values were higher than the permissible limits as recommended by World Health Organization 2006. The results also depicted significant loading of pollution parameters in wastewater from the sugar company into River Nzoia (Akali et al., 2011).

In a study done in India on heavy metal ion pollution of ground water sources by municipal solid waste dumping at Naregoan municipal, clearly pointed out that the concentration of the metal ion was increasing with respect to the vicinity to the dumping site and continued practice of waste dumping in a similar way could result in further increments of metal ions aggregation and pollution of groundwater sources, hence precautionary measures should be immediately taken to avoid the consequences (Mohammed & Gupta, 2009).

Assessment of heavy metals pollution in water and sediments and their effects on *Oreochromis niloticus* in the North Delta lakes, Egypt was carried out (Samir & Ibrahim, 2008). Results showed that water, sediments and fish organs from Lake Manzala had greater concentrations of the studied metals than those from Lake Edku and Lake Borollus. The levels of Fe, Mn, Cd, and Pb (in Lake Manzala) and Mn and Pb in Lake Borollus were found to be above the international permissible limits in water. In sediment samples Mn (in Lake Edku) and Cd (in Lake Manzala) recorded higher values than the recommended levels. Gills and liver of Niloticus contained the highest concentration of most of the detected metals, while muscles appeared to be the least preferred site for the bioaccumulation of metals (Samir & Ibrahim, 2008).

During a study in Cairo, Egypt, to determine heavy metals in drinking water and their environmental impact on human health, the results showed that there is a relationship between chronic diseases and the geological environment (Hanaa & Azza, 2000). A strong relationship between contaminated drinking water with heavy metals from some of the Great Cairo Cities (Egypt) and chronic diseases such as renal failure, liver cirrhosis, hair loss, and chronic anemia were identified in this study. These diseases were apparently related to contaminated drinking water with heavy metals such as Pb, Cd, Cu, Mo, Ni, and Cr. Renal failure was found to be due to contamination of drinking water by lead and cadmium, whereas liver cirrhosis was linked to copper and molybdenum, hair loss to nickel and chromium, and chronic anemia to copper and cadmium (Hanaa & Azza, 2000).

A study was carried out for two years in Offa, Kwara State, Nigeria to investigate the variations in selected physico-chemical factors that determine the water quality of Oyun Reservoir, for drinking and fish production (Moshood, 2008). The ranges of temperature, transparency, pH, conductivity, total dissolved solids, dissolved oxygen, nitrate, phosphate, chemical oxygen demand, total alkalinity, total hardness, calcium, magnesium, silica, sulphate, carbon dioxide were found to be comparable to those reported for other African reservoirs except for nitrogen and phosphate which were found in higher concentration above freshwater limits. Runoff of nitro-phosphate and sulphate fertilizers from nearby farm lands and washing of cows dung from the watershed into the reservoir were found to have caused cultural eutrophication in the reservoir. The eutrophication, with time, will affect the water quality and fish production in the reservoir. The study concluded that Oyun reservoir had excellent water quality, high ecological status and passed chemical status. It was recommended that eutrophication which was noticed to be a threat to the water quality should be arrested at the nick of time through denitrification and nutrient control to halt the degradation of the water (Moshood, 2008).

1.3 Analytical Techniques

1.3.1 Flame Photometry

1.3.1.1 Principles of Flame Photometry

Flame photometry is based on measurements of intensity of radiation emitted when gaseous metallic atoms emit radiation. The wavelength of colour emitted is a characteristic of that element and intensity of the colour emitted give the concentration of the element in the sample. The intensity of emission is directly proportional to the concentration of the analytes in the solution being aspirated. When a solution containing a suitable compound of the metal to be investigated is aspirated into a flame, evaporation of solvent occurs leaving a solid residue. The solid is vaporized and dissociated into free gaseous atoms in the ground state. A certain fraction of these atoms can absorb energy from the flame and be raised to an excited electronic state and attain a condition in which they radiate energy. The required spectral emission is isolated by means of a filter, and its intensity measured by photosensitive detector coupled to an amplifier. Figure 1.1 shows flame photometer instrumentation (Skoog, West, Holler & Crouch, 2008).

1.3.1.2 Flame Photometer Instrumentation

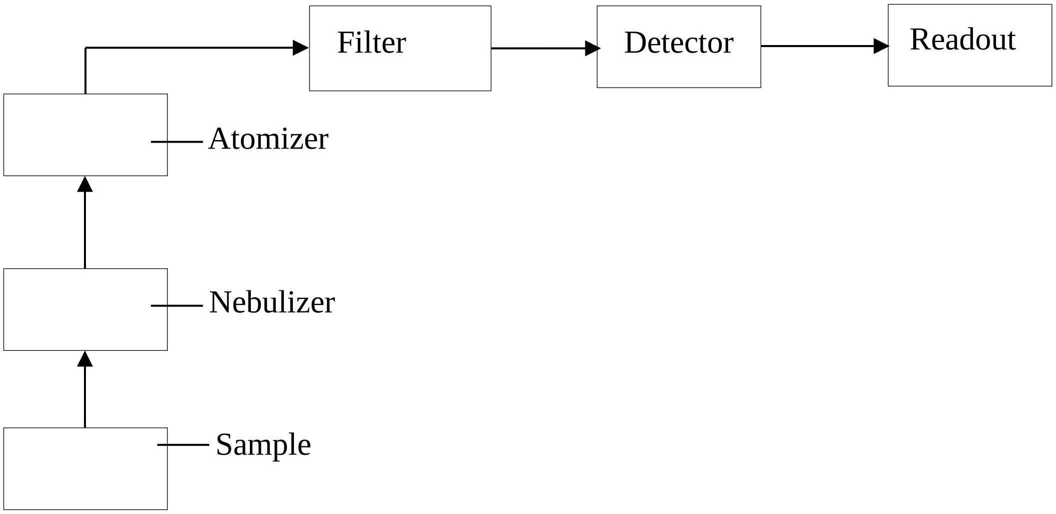

Figure 1.1: **Block diagram of a flame photometer (Skoog et al., 2008).**

1.3.1.3 Application

Flame Photometry is used specifically for analysis of alkali metals namely sodium, potassium and lithium since these metals are easily excited by low temperature flames. Each member of these groups therefore emit the characteristic colour which is unique to that element. Flame photometer is a simple and cheap instrument (Daniel, 2010).

1.3.2 Atomic Absorption Spectroscopy

1.3.2.1 Principle of Atomic Absorption Spectroscopy

An absorption spectrum is produced when electrons are excited from a lower to a higher energy level. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. If light from the emission spectrum of an element is passed through a sample, it is absorbed if it meets atoms of the same element in its path. The degree of absorption gives a measure of the concentration of the atoms present in the sample. Absorption spectroscopy quantifies the absorption of ground state atoms in the gaseous state. The analyte concentration is determined from the amount of absorption. Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration. The absorption follows Beer-Lamberts law, $A = \varepsilon l c$, ……………………………………equation 1, Where ε is the molar absorptivity in $M^{-1}cm^{-1}$, l is the pathlength in centimeters and c is the concentration of atoms in moles per liter (Skoog et al., 2008, McMahon, 2007, Nollet, 2011).

1.3.2.2 Atomic Absorption Instrumentation

In order to analyze a sample for its atomic constituents, it has to be atomized. The atomizers most commonly used nowadays are flames, electrothermal (graphite tube), and hydride generation atomizers. The atoms should then be irradiated by optical radiation, and the radiation source is an element-specific line radiation source or a continuum radiation source (e.g. hollow cathode lamp or an electrodeless discharge lamp). The radiation then passes through a monochromator which separate the element-specific radiation from any other radiation emitted by the radiation source, which is finally measured by a detector. The source of energy for free atom production is heat, most commonly in the form of an air/ acetylene or nitrous-oxide/acetylene flame (Nielsen, 2010). A pneumatic analytical nebulizer aspirates the sample solution and convert into an aerosol, which is introduced into a spray chamber. It is mixed with the flame gases and conditioned in a way that only the finest aerosol droplets (< 10 μm) enter the flame and about 1-2 % of the aspirated sample solution reaches the flame. On top of the spray chamber is a burner head that produces a flame that is laterally long (usually 5–10 cm) and only a few millimeters deep. The radiation beam passes through this flame at its longest axis, and the gas flow-rates may be adjusted to produce the highest concentration of free atoms. The burner height may also be adjusted, so that the radiation beam passes through the zone of highest atom cloud density in the flame, resulting in the highest sensitivity (Gary, 2004)**.** A schematic diagram of an AAS instrument is shown in figure 1.2 below.

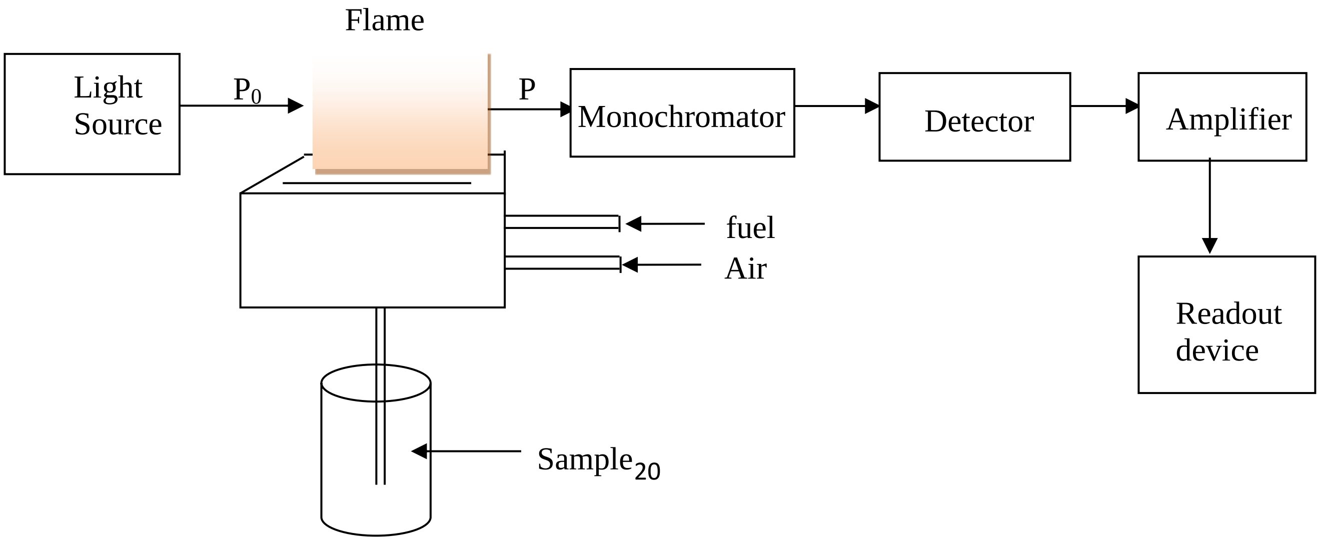

Figure 1.2: **Block diagram of a flame atomic absorption spectrometer (Skoog et al., 2008)**

1.3.2.3 Applications

Flame Atomic Absorption Spectroscopy is used for the determination of almost all metals, metalloids and some non-metals (Boron, Silicon, and Phosphorous). Atomic Absorption Spectrometry has become valuable method for trace element analysis because of its high specificity; low detection limits, easy to use, and low running costs. Atomic absorption spectrometry is generally accepted as one of the most suitable method for single element analysis of trace elements in various kinds of material. Flame Atomic Absorption Spectroscopy is a fast analysis (10-15 seconds per sample per element), has very good precision (1-5%), moderate interferences that can be easily corrected, easy automation of the measurements and relatively low cost. Atomic Absorption Spectrometry has many other uses in different areas of Chemistry such as; clinical analysis: analyzing metals in biological fluids and tissues such as whole blood, plasma, urine, saliva, brain tissue, liver, muscle tissue, semen, pharmaceutical manufacturing processes, minute quantities of a catalyst that remain in the final drug product and analyzing water for its metal content (Skoog et al., 2008).

1.3.3 Ultraviolet/Visible Absorption Spectroscopy

1.3.3.1 Principles of UV-VIS Absorption Spectroscopy

Molecules containing π-electrons or non-bonding electrons (n-electrons) can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The most probable transition would appear to involve the promotion of one electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), but in many cases several transitions can be observed, giving several absorption bands in the spectrum figure 1.3 (Subodh, 2006).

Absorption spectroscopy uses electromagnetic radiations between 190 nm to 800 nm and is divided into the ultraviolet (UV, 190-400 nm) and visible (VIS, 400-800 nm) regions, (Subodh, 2006). Energy absorbed in the UV region produces changes in the electronic energy of the molecule. As a molecule absorbs energy, an electron is promoted from an occupied molecular orbital (usually a non-bonding n or bonding π orbital) to an unoccupied molecular orbital (an antibonding π∗ or σ* orbital) of greater potential energy as shown in figure 1.3 (Subodh, 2006).

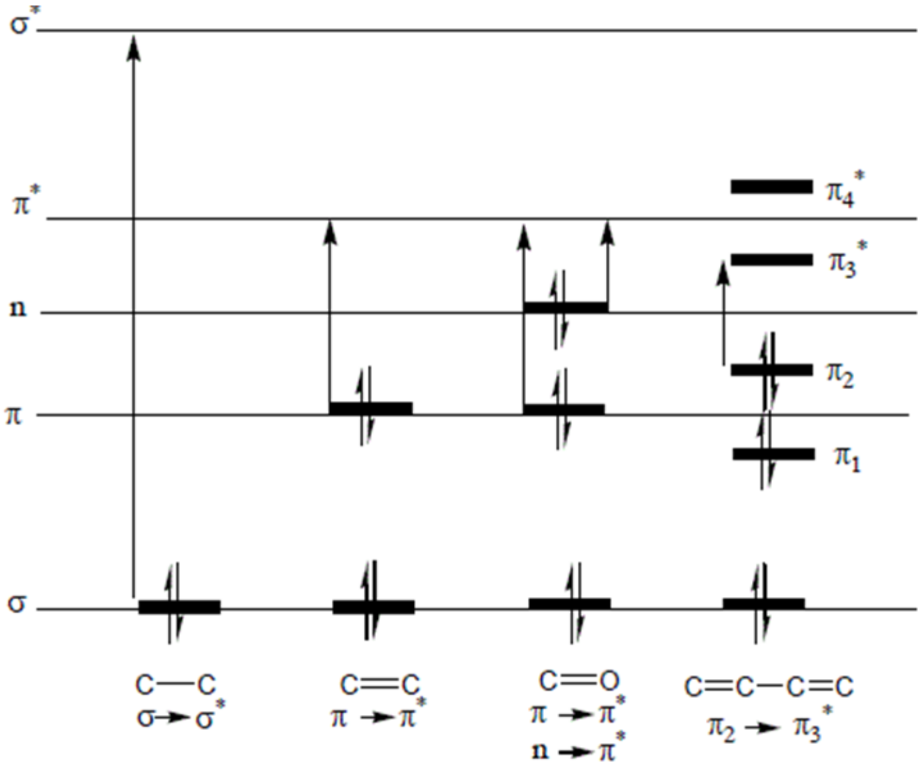

Figure 1.3: **Relative Energies of Orbitals Electronic Spectroscopy of Organic Molecules. (Skoog et al., 2008).**

In Absorption Spectrophotometry light falling on the absorbing medium may be reflected, transmitted, or absorbed, though the effect of reflection is usually eliminated by means of a comparison cell. Quantitative absorption measurements are based on relationships derived from two fundamental laws. Lambert's Law states that the proportion of light absorbed by a substance is independent of the intensity of the incident. Beer's Law**,** derived from quantitative work on the absorption of red light by aqueous solutions, states that the absorption is proportional to the total number of molecules in the light path. Combining the algebraic form of these two laws we obtain the expression, the Beer-Lambert law $A = log_{10}\left(\frac{I_o}{I}\right) = \varepsilon CL,$ ……………………......equation 2,

Where A is the measured absorbance, I_O is the intensity of the incident light at a given wavelength, I is the transmitted intensity, l the path length through the sample, and c the concentration of the absorbing species. For each species and wavelength, ε is a constant known as the molar absorptivity or extinction coefficient. UV/Vis spectrophotometer measures the intensity of light passing through a sample and compares it to the intensity of light before it passes through the sample (I_o). The ratio I/I_o is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance: A = -log (%T/100%) …equation 3. Beer's Law is usually regarded as being valid at least in dilute solutions; where deviations occur it can usually be explained by a change in molecular species due to association, ionization or other phenomena (Skoog et al., 2008).

1.3.3.2 UV-VIS Instrumentation

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector. The radiation source is often a tungsten filament (300-2500 nm), a deuterium arc lamp, which is continuous over the ultraviolet region (190-400 nm), Xenon arc lamp, which is continuous from 160-2000 nm; or more recently, light emitting diodes (LED) for the visible wavelengths. The detector is typically a photomultiplier tube, a photodiode, a photodiode array or a charge-coupled device (CCD). Monochromator filter the light so that only light of a single wavelength reaches the detector at one time (Daniel, 2010).

A spectrophotometer can be either single beam or double beam. In a single beam instrument, light passes through the sample cell. I_o is measured by removing the sample. In a double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference while the other beam passes through the sample. The reference beam intensity is taken as 100% transmission (or 0 absorbance), and the measurement displayed is the ratio of the two beam intensities. In other instruments, the two beams pass through a beam chopper, which blocks one beam at a time. The detector alternates between measuring the sample beam and the reference beam in synchronism with the chopper. There may also be one or more dark intervals in the chopper cycle. In this case, the measured beam intensities may be corrected by subtracting the intensity measured in the dark interval before the ratio is taken. A Schematic diagram of UV-VIS Spectrophotometer is shown below figure 1.4(Daniel, 2010).

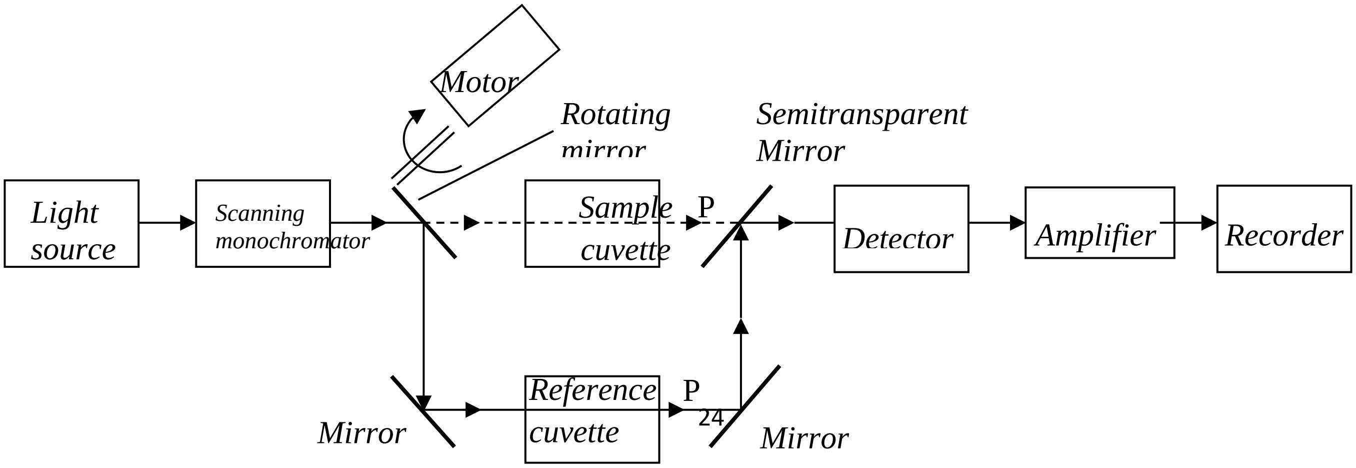

Figure 1.4: Block diagram of a Double Beam Spectrophotometer (Daniel, 2010).

1.3.3.3 Applications

UV/Vis spectroscopy is routinely used in Analytical Chemistry for the quantitative determination of different analytes, such as transition metal ions, highly conjugated organic compounds, and biological macromolecules. Spectroscopic analysis is commonly carried out in solutions but solids and gases may also be studied. Ultraviolet and visible spectrometers have been in general use for the last 35 years and over this period have become the most important analytical instrument in the modern day laboratory. In many applications other techniques could be employed but none rival UV-Visible spectrometry for its simplicity, versatility, speed, accuracy and cost-effectiveness.

1.3.4 Potentiometric analysis

The potentiometric method is based upon measurements of the potential of the electromotive force of a galvanic element. Direct potentiometric determinations are almost always performed using ion selective electrodes (ISEs), which are capable of rapid and selective measurements of analyte concentration.

1.3.4.1 Principles of Ion Selective Electrode

Ion-selective electrode potentials vary in response to changes in the concentration of a specific analyte in solution or in the gas phase. The membrane potential is selective toward a given ion or ions, just as the potential of the glass membrane of a conventional glass electrode is selective toward hydrogen ions. None of these electrodes is specific for a given ion, but each will possess a certain selectivity toward a given ion or ions, so they are referred to as an Ion-Selective Electrodes (ISEs). Ion-Selective Electrodes are membrane based electrodes that measure a specific ion in aqueous solutions. When the membrane of the electrode is in contact with a solution containing the specific ion, a voltage, dependent on the concentration of that ion in solution, develops at the membrane. The cell voltage is the difference between the variable potential that reflects changes in the analyte activity and the constant potential from the reference electrode (Daniel, 2005).

The voltage developed between the sensing and the reference electrodes is a measure of the concentration of the reactive ion being measured. As the concentration of the ion reacting at the sensing electrodes varies, so does the voltage measured between two electrodes.

As described in the Nernst equation (Daniel, 2005). ISE response is a linear equation:

Thus at $25^0 C, E_{meas} = constant + \frac{0.05916}{n} log_{a\ ion\ outer}$, …………………………....equation 4.

For fluoride ion solutions at 25^0C and constant ionic strength,

$E_{meas} = constant - 0.05916 log Y_{F-} - 0.05916\ log[F-]_{sample} =$

$constant\ 0.05916 log[F-]_{sample,}$ ……………………………………………………equation 5.

Thus, for an ideal fluoride ISE, the cell potential is linearly related to the logarithm of the fluoride ion concentration. When the ionic strength of all standards and samples is constant, the response of a real fluoride ISE is described by a similar relationship.

$E_{meas} = constant - \beta(0.05916)\ log[F -]_{sample}$,… ……………………equation 6.

Where β is the electromotive efficiency and typically has a value very close to unity (> 0.98).

Using the voltage reading, the natural logarithms of concentration of the specific ion can be determined. The ion concentration can be determined from the natural logarithms of concentration. (Daniel, 2005). A schematic diagram of an Ion selective electrode is shown below figure 1.5.

1.3.4.2 Instrumentation

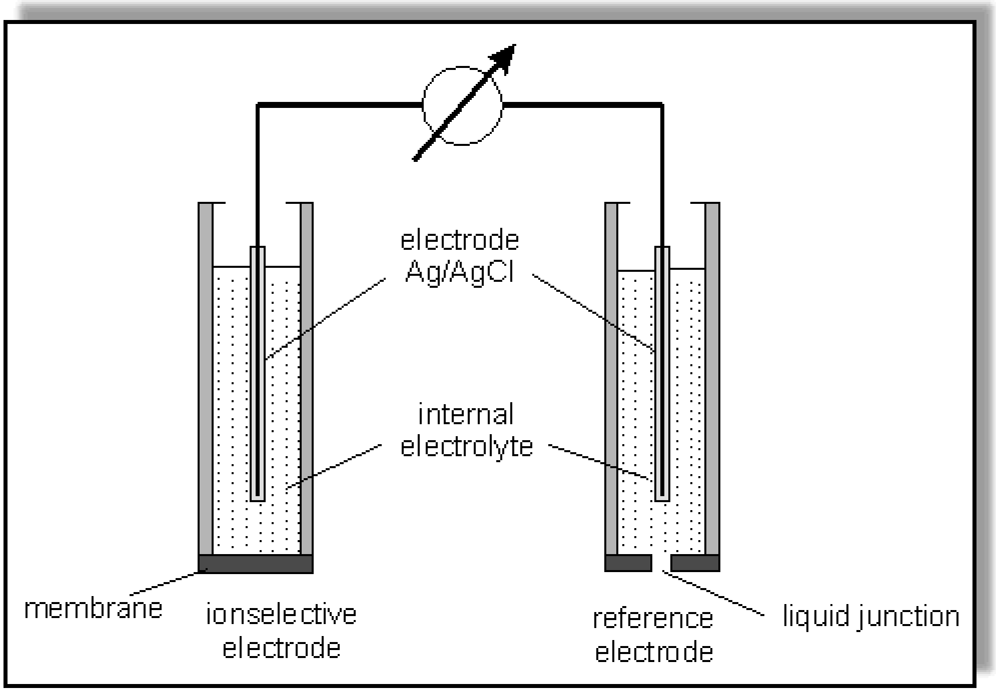

Figure 1.5: **Schematic representation of reference and an Ion-Selective Electrode (Daniel, 2010).**

The ion selective electrode consist of ion-sensing part consists of a membrane (which may be plastic, glass or an ionic crystal) which has sites which are capable of adsorbing the analyte ion. On either side of the membrane is a solution containing the ion of interest: one of these is the test solution, the other is a standard HCl solution (saturated in KCl, and AgCl if an Ag/AgCl internal reference electrode is employed) in the bulb (typically 0.1 M). Inside the electrode body, there is an electrical connection, a wire or a reference electrode to monitor the response from the membrane. In most pH electrodes the external reference electrode is physically enclosed with the glass electrode, meaning that only one electrode unit is required. Most common indicator electrodes are made of platinum, which is relatively inert. A metal electrode works best when its surface is large and clean. Its purpose is mainly to transmit electrons to or from a species in solution. (Daniel, 2005).

1.3.4.3 Applications

Ion-selective electrodes are widely used for analysis in the environmental, food, health, medicine and biochemical areas. The most common is the pH electrode, which responds to free H^+, and other commonly used electrodes are for fluoride, nitrate, calcium, chloride, sodium and carbon dioxide. The development of potentiometric ion-selective electrode has a wide range of applications in determining ions in water and other media. These electrodes are relatively free from interferences (colour or turbidity) and provide a rapid, convenient and non-destructive means of quantitatively determining numerous important anions and cations. The use of ion-selective electrodes enables the determination of very low concentrations of desired ions (Daniel, 2005).

1.4 Problem Statement

Mathioya River water support many families for both human, animal drinking and for watering food crops that are supplied throughout the county and Nairobi City. Piped chlorinated water supply in Murang’a County is inadequate and most people use the untreated Mathioya river water for domestic purposes, hence the need to ascertain the quality of the river water. Effluents from motor vehicle repair garages in the town, solid wastes, sewage effluents, and sanitation facilities are not adequate in this area and in most cases wastes from these sources reach River

Mathioya and this is a potential source of heavy metal pollution. The rising population has also resulted into deforestation due to demand for more land for farming and grazing which has rendered soil loose and hence increased soil erosion into the river, leading to further pollution.

Fertilizers from farming activities along the river through leaching may find their way into River Mathioya. Despite this, no comprehensive study has been reported on the quality of River Mathioya water therefore the research findings will be used as reference in similar future studies. In view of the potential health risks to man through the consumption of polluted water, it is important to constantly assess the pollution status of the river and disseminate the findings to the users and agencies that monitor environmental pollution such as NEMA, Kenya

1.5 Justification of the Study

Polluted water causes environmental health effects with the occurrence of water-borne diseases, for example, typhoid and cholera, and chemical poisoning in humans and animals; aesthetic effects leading to loss of scenic beauty with water becoming unsuitable for recreation activities; and high cost of water supply as polluted water is expensive to treat. Heavy metals easily accumulate along food chains leading to health problems such as cancer, brain disorder, kidney damage, renal damage and lethal to fish and other aquatic animals and plants. In addition, water resources in Kenya are under pressure from agricultural chemicals (fertilizers and herbicides) and urban and industrial wastes. The situation is much worse in the informal settlements in the urban areas due to lack of proper sanitation and sewerage systems. Different research studies have indicated increased cases of cancer victims that are attributed to heavy metals from polluted water. Deterioration of the quality of the aquatic environment leads to deoxygenation, eutrophication, siltation, habitat modification and toxicity of the water. Due to the above effects of polluted water, river Mathioya is likely to be polluted and therefore there is need to determine the quality of its water so that recommendations can be made on the best disposal methods to reduce water pollution. The importance of this study is to identify the sources of pollution to the river and hence recommend control measures aimed at minimizing the environmental impacts.

1.6 Hypothesis

The water quality of River Mathioya is not affected by pollution from Murang’a town, Kenya and its environs.

1.7 Objectives

1.7.1 General Objective

To assess the impact of effluents discharge from Murang’a town and its environs on the quality of water of River Mathioya, Kenya.

1.7.2 Specific Objectives

1. To determine the physico chemical parameters such as pH, TDS, TSS, DO, Temperature and Electrical Conductivity in the water samples of River Mathioya, and streams (Karii, Murari), Kenya.

2. To determine the levels of Nitrates, Fluorides and Phosphates in the water samples of River Mathioya and streams (Karii, Murari).

3. To determine the levels of Sodium, Potassium, in the water samples of River Mathioya and streams (Karii, Murari).

4. To determine the levels of Fe, Mn, Zn, Cu, Pb and Cr in the water samples of River Mathioya and streams (Karii, Murari).

5. To compare the results obtained from all the parameters determined with the WHO recommended permissible levels in drinking water.

CHAPTER TWO

MATERIALS AND METHODS

2.1 Study area

Mathioya River under study originates from the Aberdares ranges. It joins Tana River at Sagana Bridge at the borders of Muranga and Kirinyaga County. A map of Kenya showing Murang’a County is displayed in Figure 2.1 below and figure 2.2 showing streams (Murari and Karii) and Mathioya River. A comparison of the studied parameters of water samples from parts of River Mathioya and streams (Murari and Karii) in Murang’a County.

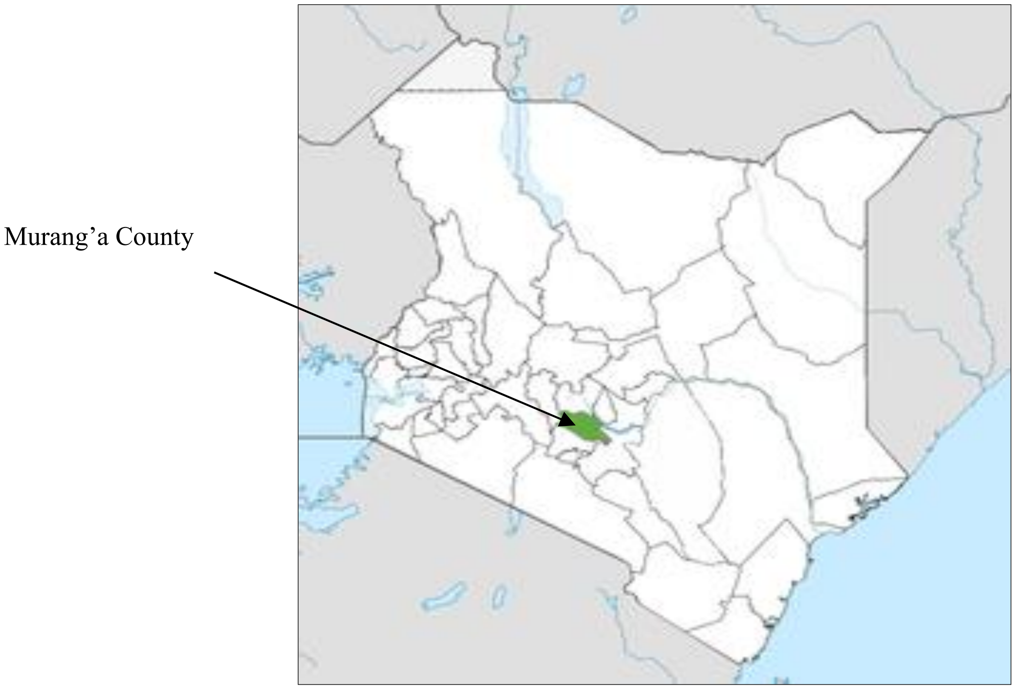

Figure 2.1: Map of Kenya showing Murang'a County

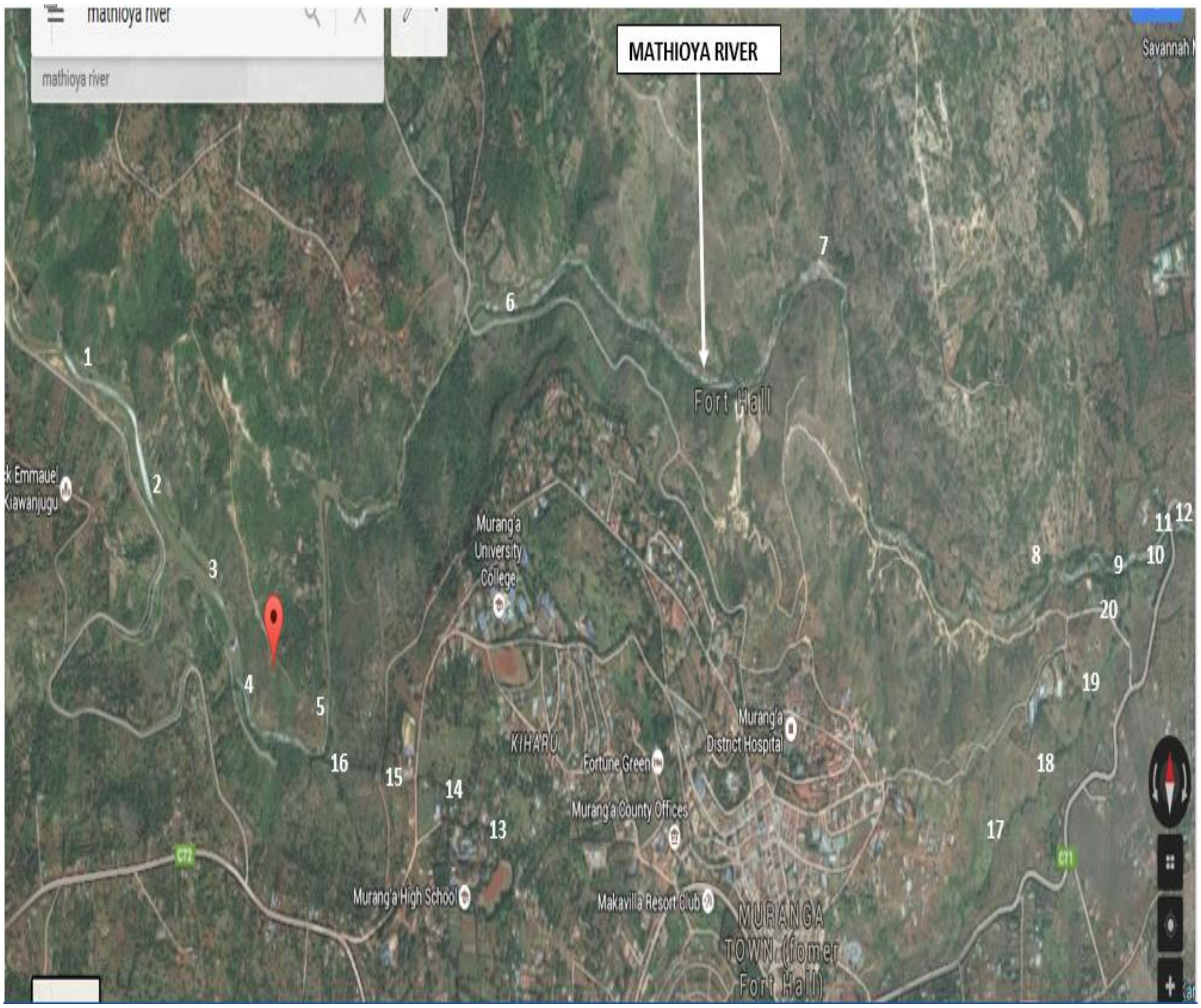

Figure 2.2: Location of Karii, Murari Streams and Mathioya River

2.2 Sample collection and pre-treatment

The sample collection design chosen was convenient sampling. Samples were collected in triplicate from twenty sampling sites along Mathioya River and streams (Murari and Karii), (Figure 2.2). The sites chosen were considered as point sources of pollution, assumed mid-point of the river, along the river and streams effluent discharge points and the source to serve as a control. The samples were collected during the wet season between April and June 2015, there were 20 sampling points along Mathioya River, Murari and Karii streams. Triplicate samples were picked from each sampling point totaling 60 samples. The samples were picked around Murang'a town, Twelve (12) samples were picked from each sampling points blocks (1-4) upstream before the town, 5-8 along Mathioya River in between Murari and Karii streams, 9-12 in Mathioya River after Karii stream, 13-16 from Murari stream and 17-20 from Karii stream. Total samples collected were 60.

2.2.1 Sampling and Storage for Phosphate and Nitrate samples

At each sampling site, plastic bottles were rinsed with river water before retaining a sample. The samples were then tightly caped and placed in a fringe container and immediately transported to the laboratory. They were filtered using whatman filter papers to avoid interference due to turbidity and color and then kept in a refrigerator at a temperature of 4^0C.

2.2.2 Sample collection for metal analysis

At each sampling site, the bottles were rinsed with river water before sampling. Pre-cleaned polyethylene sampling bottles were immersed to about 10 cm below the water surface. Three each of 500 mL of water samples were taken at each sampling site, immediately acidified with 5mL concentrated nitric acid to a pH of less than 2 and transported to the laboratory. The samples were filtered through a 0.45 μm micro pore membrane filter and kept at 4°C (Ozturk et al., 2009).

2.3 Cleaning of Apparatus

Plastic reagent bottles were used for sample collection. Before use they were washed with 10 % nitric acid and rinsed with distilled water. All glassware were washed and rinsed with 10% HCl followed by distilled water to avoid metal contamination.

2.4 Chemicals and Reagents

Chemicals and reagents used were of analytical grade. They included; nitric acid (37%), hydrochloric acid (70%), sulphuric acid (98%), distilled water, hydrogen peroxide, zinc nitrate, ammonium chloride potassium dihydrogen orthophosphate, lead (II) nitrate, sodium fluoride, sodium chloride, potassium chloride, copper (II) sulphate, lead nitrate, chromium (VI) oxide, potassium dichromate, lead (II) nitrate, manganese (II) chloride, zinc chloride and sodium hydroxide pellets (purity 98%). The chemicals were supplied by Sigma Laboratories in the United States of America and Reagent Chemical Services (UK).

2.4.1 Preparation of Phosphate Reagent

70 mL 2.5M H_2SO_4 was diluted to 500 mL with distilled water; 1.3715 g potassium antimonyl tartrate dissolved in 400mLdistilled water in a 500-mL volumetric flask and dilute to volume and stored in a glass-stoppered bottle; 20 g ammonium molybdate $(NH_4)_6Mo_7O_{24}\ .4H_2O$) was dissolved in 500 mL distilled water, and stored in a glass-stoppered bottle; 1.76 g, 0.1 M ascorbic acid were dissolved in 100 ml distilled water. The above reagents then combined into 100 mL as

follows : 50 mL 2.5M H_2SO_4, 5 mL potassium antimonyl tartrate solution, 15mL ammonium molybdate solution, and 30 mL ascorbic acid solution were mixed together into a reagent. Combined reagent which was shaken and left to stand for 4 hours (APHA, 2005).

2.4.2 Preparation of Total Ionic Strength Adjustment Buffer (TISAB)

Approximately 500 mL distilled water were put into a 1000 mL volumetric flask, 57 mL glacial acetic acid added then 58g of NaCl and 4g of 1,2 cyclohexylenedinitrilotetraacetic acid (CDTA) added and stirred to dissolve, cooled in a water bath. For adjusting pH to between 5.0 to 5.5; 5M NaOH was slowly added with stirring and topped to the mark with distilled water (APHA, 2005).

2.5 Instrumentation

2.5.1 The pH, temperature, TSS, DO, TDS and conductivity meter

HANNA pH, temperature, TDS and conductivity meter (model H1991000) Jenway, UK, digital potable dissolved oxygen meter HACH DO175. Win lab meter (Model WH200202) for the TSS were used.

2.5.2 Ion-Selective Fluoride Meter

Fluoride was measured using a meter with an ion selective combination electrode, model 96-09Thermo, manufactured by Orion Research of Beverly Mass Company, USA.

2.5.3 Flame Photometer

Flame Emission Photometer model FP6410 from Scientific Products of Halstead, Essex, England, and using air- acetylene fuel fitted with sodium, potassium and lithium filters.

2.5.4 UV-VIS Spectrophotometer

Beckman DU640UV/Vis Doublebeam spectrophotometer from Arthur H. Thomas Company.

2.5.5 Flame Atomic Absorption Spectrophotometer

Flame Atomic Absorption Spectrophotometer (AAS - Shimadzu AA 7000) model with an air/nitrous-acetylene burner for flame with deuterium lamp for background correction.

2.6 Preparation of Standards

2.6.1 Preparation of Phosphate Standards

The standards were prepared according to the Standard Methods for the Examination of Water and Waste Water (APHA, 2005). 1000 ppm of standard phosphate solution was prepared by weighing exactly 1.4329 g of analytical grade potassium dihydrogen orthophosphate and diluting to 1000 mL in a standard volumetric flask using distilled water. Using 1mL pipette, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mL of the standard phosphate solutions were each accurately pipetted into a 100mLvolumetric flasks topped to the mark with the combined reagent to make solutions equivalent to 1-6 ppm. A mixture of blank with the combined reagent were used to make photometric readings for the calibration curve. A plot of absorbance versus phosphate concentration was obtained.

2.6.2 Preparation of Nitrate Standards

A stock solution of 1000ppm nitrate standards was prepared from lead (II) nitrate by dissolving 5.325 g of lead (II) nitrate in distilled water and made into one litre. The stock solution was used to prepare a series of standards for the calibration curve (APHA, 2005).

2.6.3 Preparation of Fluoride Stock Solution

Flouride stock solution was prepared by dissolving 0.5476 g anhydrous sodium fluoride (NaF) in distilled water and diluting to 1 litre.

2.6.4 Preparation of Sodium and Potassium Standards

Sodium and Potassium stock solutions were prepared by dissolving appropriate amounts of analytical grade salts of Sodium chloride and potassium chloride in distilled water. The working standard solutions ranging from 0.50 mg/L to 10 mg/L of the metals was prepared by appropriate dilution of the standards and was used to prepare the calibration curves (Appendices 1 and 2).

2.6.5 Preparation of Heavy Metal Standards

Metal salts of Analar grade (99.9%) for each metal were first dried at 105°C in an oven, then cooled in the desiccators prior to weighing. Stock solutions (1000 mg/L) were prepared by dissolving appropriate amounts of analytical grade salts of copper (II) sulphate, chromium (VI) oxide, iron (II) chloride, lead (II) nitrate, manganese (II) chloride and zinc chloride in distilled water. Then the working standard solutions ranging from 0.1 mg/L to 100 mg/L of the metals were prepared by appropriate dilution and were used to prepare the calibration curves. For each metal determination, the standards prepared were aspirated into the flame atomic absorption spectrometer and the absorbance values obtained were used to plot the calibration graph of absorbance versus concentration of the standards (Appendices 3, 4, 5, 6, 7 and 8).

2.7 Experimental procedure

All the analysis were determined according to the American Public Health Association Standard Methods for Examination of Water and Wastewater (APHA, 2005).

2.7.1 Determination of pH, temperature, TSS, DO, TDS and EC

A pre-calibrated HANNA pH, Temperature, TSS, DO, TDS and Conductivity Meter (model H1991000) was used for pH, temperature, Total Dissolved Solids, Total Suspended Solids and Electrical Conductivity measurements. The pH of each water sample was measured by inserting the meter probe into the water sample immediately after collection from the river. It was rinsed and left standing in distilled water before being used for further pH measurements. Temperature, total Dissolved Solids and conductivity readings were also taken at the same time as pH. Dissolved Oxygen was measured using a digital potable dissolved oxygen meter and Win lab meter was used to determine the TSS. These parameters were measured on site.

2.7.2 Determination of Phosphates

50.0 mL of the sample was pipetted into a clean, 250-mL volumetric flask. A drop (0.05 mL) phenolphthalein indicator was added and 2.5 M H_2SO_4 solution added dropwise to develop the red color after which 8.0 mL combined reagent (2.41) was added and mixed thoroughly. After 10 min but no more than 30 min, absorbances was measured for each sample at 880 nm, using reagent blank as the reference solution (APHA, 2005).

2.7.3 Determination of Nitrates

Nitrate was determined using UV-Vis Spectrophotometry. The procedure involved addition of 1 mL of concentrated hydrochloric acid into 50 mL of the samples to decompose the carbonates. Samples absorbance were read at 220 nm from the calibration curve, (APHA, 2005).

2.7.4 Determination of Fluorides

25.00 ml of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ppm fluoride standard solutions were pipetted into a 100 mL volumetric flask and after addition of 50 ml of TISAB solution reagent, it was diluted to the mark with deionized water and then stoppered and thoroughly mixed. Then 50 mL of the sample was pipetted into a 100 mL volumetric flask and topped to the mark with TISAB solution and stirred. The fluoride ion selective electrode was connected to a pH meter and set to the millivolts. The electrode was rinsed with deionized water and blot dried and lowered into the standard solutions, after 5 minutes readings were attained and recorded. After taking readings for all the standard solutions, a calibration curve was prepared by plotting the relative mV versus the logarithm of the concentration of the standards and the slope (S) was obtained. When a stable reading was displayed, the pontential (E_1) in millivolts were recorded. 10.0 ML of a 8.0 ppm fluoride standard solution were pipetted into the beaker and again stirred thoroughly. When a stable reading was displayed, the new pontential (E_2) were recorded. The first reading (E_1) were subtracted from the second(E_2) to find change in pontential, ΔE**.** Above procedure was repeated for all the samples. The concentration of fluoride mg/L in the water samples was calculated as follows; C sample= QC standard

Where, C sample = sample concentration

QC standard =Standard concentration

$Q=P/ [1+P)10^{\Delta E/S}]-1$

S = slope of the electrode

P = Volume of standard **/**volume of sample.

$\Delta E = E_2 - E_1$

2.7.5 Determination of Sodium and Potassium

Concentration of Sodium and potassium ions were determined by Flame Emission Photometry. At set experimental conditions for sodium and potassium. Standards of sodium and potassium were used to calibrate the Flame Photometer using wavelengths of 589 and 768 nm respectively. The samples concentrations were obtained from the standard calibration curve.

2.7.6 Determination of Heavy Metals

Water samples were digested in triplicates according to the method described by (APHA, 2005). 10 mL of the filtered water were digested with 5 ml of conc. HNO_3 at 100°C with the addition of 3 drops of hydrogen peroxide until there were no brown fumes. The mixture was filtered using Whatman 0.45µm filter paper in a 100 Ml volumetric flask and topped with distilled water for aspiration into the Flame Atomic Absorption Spectrophotometer. The sample solutions were then introduced into the flame and their absorbance values were used to deduce the concentration by interpolation.

CHAPTER THREE

RESULTS AND DISCUSSION

3.1 Physico-Chemical Parameters

3.1.1 pH

The pH values ranged from 6.70 ± 0.13 in sampling point 17 to 7.98 ± 0.09 in sampling point 5 as shown in Table 3.1 and Figure 3.1. The pH levels were within the WHO optimum limits for drinking and portable water, which is 6.5 and 8.5 (WHO, 2006). All the mean values of pH obtained for all the samples fell within the WHO range but were slightly above the natural background level of 7.0. This increase in pH of the water samples above the natural background levels may be due to the presence of dissolved carbonates and bicarbonates present in the water, which affects the pH of surface water (Araoye, 2009 & Mustapha, 2009). The increase in pH can also be attributed to organic pollution and the domestic waste discharge draining into the river system as it traverses the habited areas, Araoye (2009). Similar findings were also reported during study on the seasonal variation of pH and dissolved oxygen concentration in Asa lake

Ilorin, Nigeria (Araoye, 2009 & Mustapha, 2009). The pH also influences other parameters like conductivity, bicarbonates, chlorides, salinity, phosphates, hardness and magnesium in water (Araoye, 2009). There was significant difference between the levels of pH across all the sampling points according to Student-Newman-Keuls statistical test as shown in Appendix 11.

Table 3.1: Physico-chemical Parameters

Sampling point	Number of samples (n)	Temp. ^{o}C	EC (µS/cm)	DO (mg/L)	pH	TDS (mg/L)	TSS (mg/L)
1.	3	22.53±0.45	63.51±0.26	8.79±0.18	7.43±0.09	38.32±0.28	45.26±0.69
2.	3	23.23±0.05	63.75±0.10	8.68±0.16	7.41±0.08	38.69±0.11	43.37±0.86
3.	3	22.73±0.17	64.10±0.11	8.24±0.16	7.46±0.09	37.44±0.47	39.38±0.89
4.	3	21.33±0.05	64.20±0.05	7.37±0.13	7.46±0.11	36.92±0.16	43.12±0.72
5.	3	22.77±0.12	64.60±0.14	5.32±0.16	7.98±0.09	36.80±0.10	47.47±0.82
6.	3	20.27±0.05	64.66±0.19	5.39±0.14	7.67±0.09	36.60±0.16	46.44±0.59
7.	3	20.50±0.22	65.40±0.09	5.31±0.10	7.76±0.15	37.96±0.19	47.79±0.75
8.	3	20.07±0.12	64.32±0.06	5.24±0.14	7.67±0.08	42.83±0.09	57.09±0.81
9.	3	19.80±0.29	76.52±0.07	5.38±0.14	7.09±0.11	41.68±0.13	51.79±0.53
10.	3	20.31±0.34	77.38±0.03	5.15±0.11	7.41±0.13	40.73±0.18	54.11±0.89

11.	3	20.60±0.24	77.17±0.03	6.08±0.13	7.69±0.13	42.58±0.11	56.01±0.69
12.	3	20.40±0.08	65.21±0.07	5.21±0.10	7.63±0.07	44.56±0.17	53.43±0.74
13.	3	20.97±0.49	65.48±0.04	6.12±0.13	6.94±0.11	42.23±0.14	49.93±0.72
14.	3	20.63±0.21	65.39±0.04	4.18±0.07	6.95±0.09	50.18±0.17	50.29±0.85
15.	3	21.53±0.09	66.23±0.07	5.22±0.08	7.26±0.08	41.23±0.12	46.73±0.57
16.	3	21.40±0.08	79.19±0.06	5.10±0.12	7.25±0.09	41.31±0.12	42.85±0.59
17.	3	21.57±0.17	79.15±0.04	4.88±0.08	6.70±0.13	38.54±0.17	48.79±0.70
18.	3	21.37±0.12	80.88±0.28	4.75±0.08	6.96±0.08	38.01±0.15	48.95±0.60
19.	3	21.47±0.07	81.46±0.05	4.26±0.07	6.86±0.08	37.15±0.15	47.85±0.51
20.	3	22.08+0.35	70.26±0.89	4.33+0.08	6.91+0.12	37.12+0.16	48.54+0.63

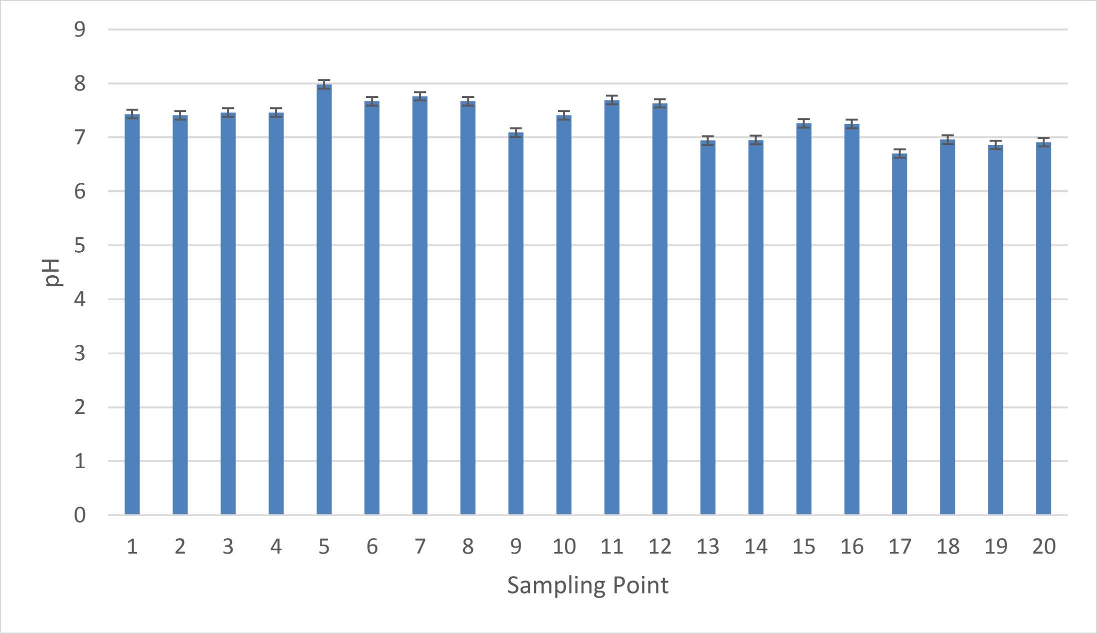

Figure 3.1: **Graph of pH levels**

3.1.2 Temperature

The average temperature ranged from 19.80 ± 0.29 ^{0}C in sampling point 9 to 22.77 ± 0.12 ^{0} C in sampling point 5 as shown in Table 3.1 and Figure 3.2. There was significant difference between the levels of temperature across all the sampling points according to Student-Newman-Keuls statistical test as shown in Appendix 11. There was a significant difference between the levels of temperature across all the sampling block but there was no significant difference between blocks 1 and 4, block 2 and 3 and block 4 and 5(Dwivedi & Pandey, 2002).

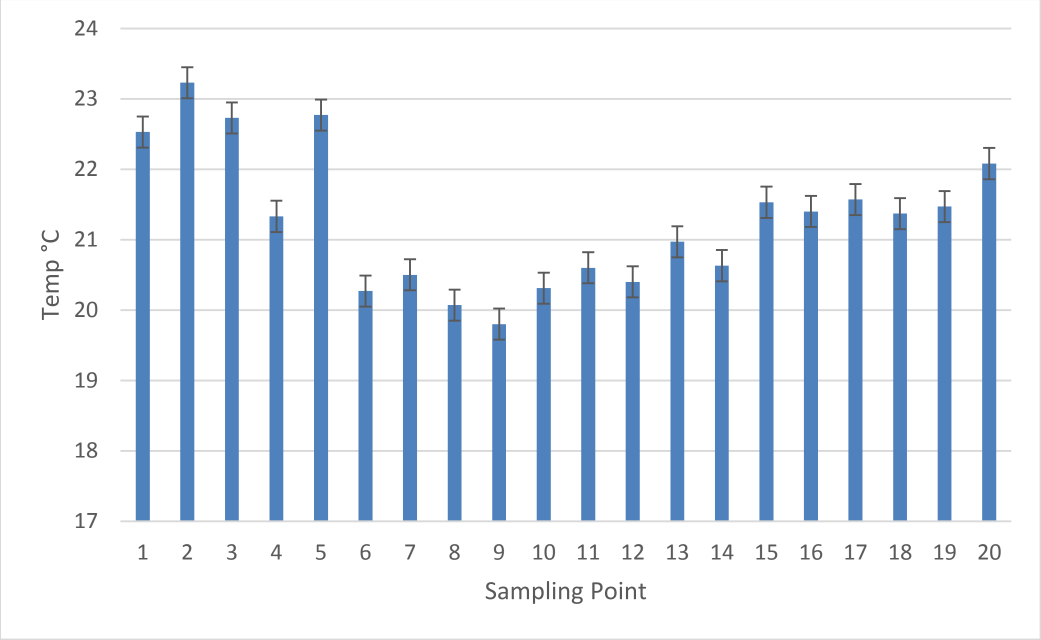

Figure 3.2: **Graph of temperature**

3.1.3 Electrical Conductivity

The electrical conductivity varied between a minimum mean of 63.51 ± 0.26 µS/cm in sampling point 1 to 81.46 ± 0.31 µScm in sampling point 19 as displayed in Table 3.1 and Figure 3.3. The WHO, 2006, limit for electrical conductivity for drinking and potable water is 700 µS/cm. All samples were within this limit. Increased concentration of cations such as calcium, magnesium and sulphate could be attributed to runoffs during the rainy period. Conductivity showed a positive correlation with total dissolved solids. Using Student-Newman-Keuls test statistical test as shown in Appendix 11, it was found out that there was significant difference between the levels of electrical conductivity across all the sampling points according to Student-Newman-Keuls statistical test as shown in Appendix $p < 0.05$ level of significance.

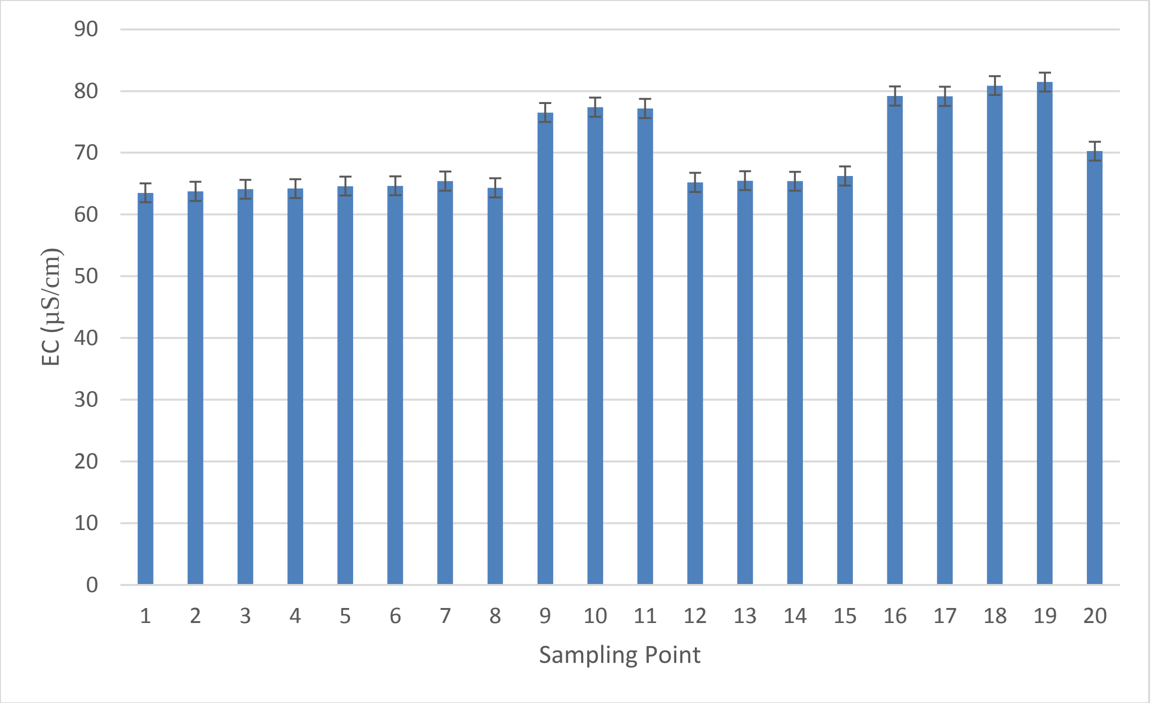

Figure 3.3: **Graph of electrical conductivity**

3.1.4 Total Suspended Solids

The total suspended solids in the sampled water ranged from 42.85 ± 0.59 mg/l in sampling point 16 to 57.09 ± 0.81 mg/l in sampling point 8 as shown in Table 3.1 and Figure 3.4. This was higher than the world health organization permissible limit of 30 mg/L. Total suspended solid contents of water depends on the amount of suspended particle, soil, silt and is directly related to turbidity of water. Disposal of sewage and industrial effluents contributes to suspended matter to rivers, (Keramat, 2008). Low level of total suspended solids were recorded for Kosi River at Uttrakhand, Iran, and the average value of TSS varies from 3 to 174 mg/l, (Keramat, 2008), which are slightly higher than River Mathioya. The higher amount of total suspended solids in the collected samples were attributed to run off from Murang'a town solid garbage dumps wastes which results in the presence of several suspended particles. There was significant difference between the levels of TSS across all the sampling points as per the Student-Newman-Keuls Statistical test at $p<0.05$ level of significance as shown in Appendix 11.

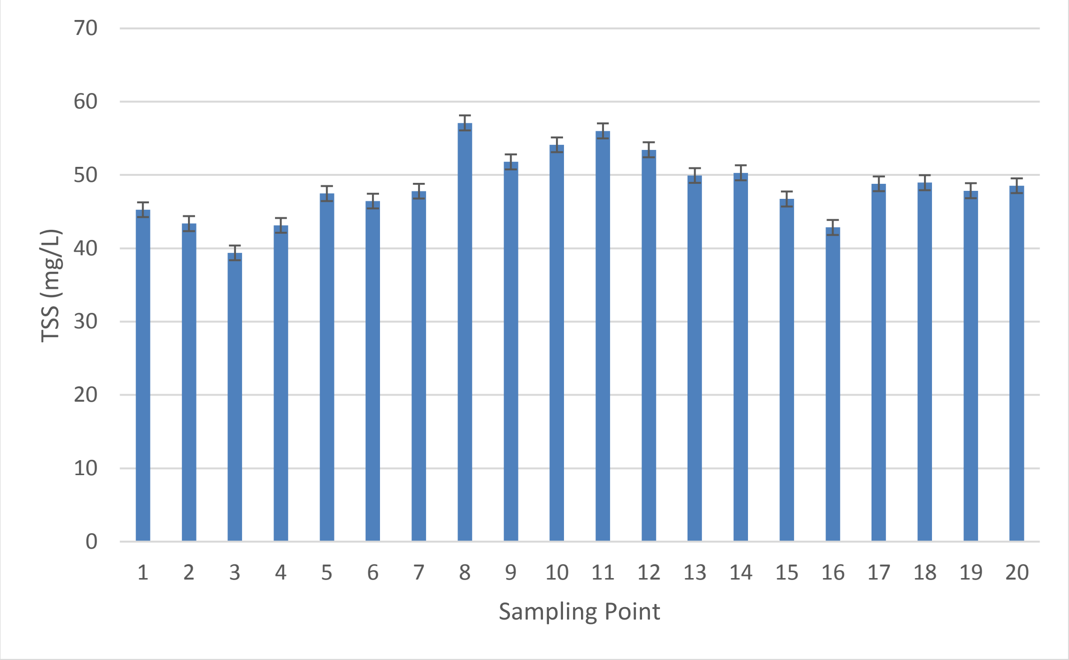

Figure 3.4: Graph of mean concentration of total suspended solids

3.1.5 Total Dissolved Solids

Total dissolved solids ranged from 36.60 ± 0.16 mg/l in sampling point 6 to 50.18 ± 0.17 mg/ l in sampling point 14 as shown Table 3.1 and Figure 3.5. Higher values of total solids could be due to the presence of silt and clay particles in the river water. The levels of TDS were within tolerable limits for drinking water they did not exceed 1500 mg/l (EPHA, 2009). The TDS values followed the same trend as electrical conductivity. A similar trend of TDS was also observed during an analytical study of heavy metals of industrial effluents at Jaipur, Rajasthan, India

(Mustapha, 2009 & Singh & Chandel, 2010). That study also observed that as electrical conductivity increased TDS values increased (Mustapha, 2009 & Singh & Chandel, 2010). Using Student-Newman-Keuls test as shown in Appendix11, it was found that there was a significant difference between the levels of TDS across all the sampling points at p< 0.05 level of significance.

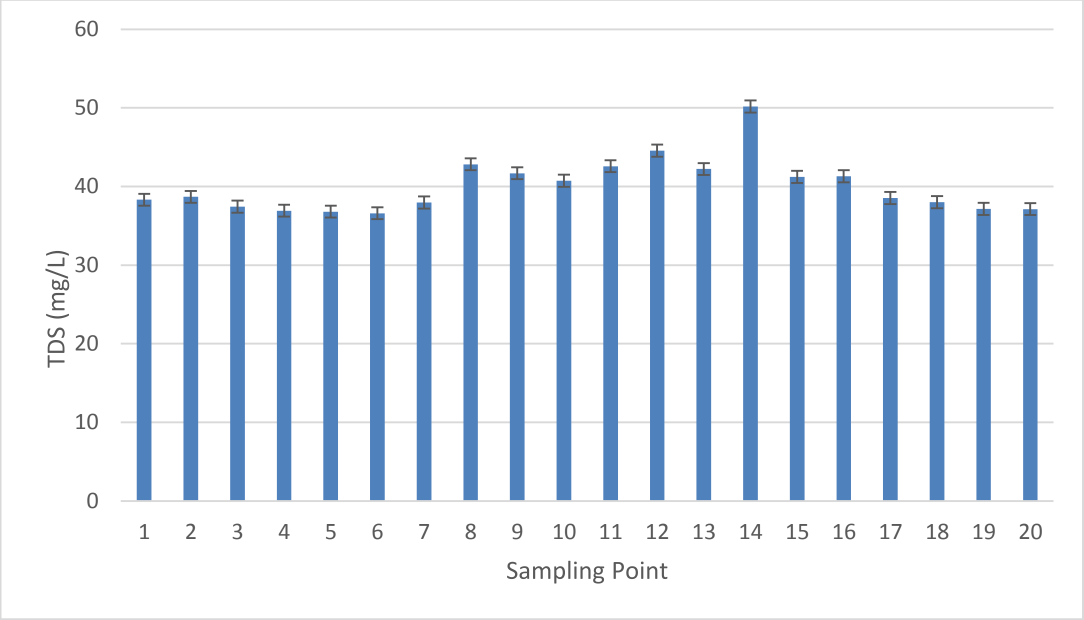

Figure 3.5: **Graph of mean concentration of total dissolved solids**

3.1.6 Dissolved oxygen

Dissolved oxygen mean concentration ranged from 4.18 ± 0.07 mg/L in sampling point 14 to 8.79 ± 0.18 mg/L in sampling point 1 as shown in Table 3.1 and Figure 3.6. The dissolved oxygen for sustaining aquatic life is 4 mg/L, while for drinking purposes, it is 6 mg/L. Dissolved oxygen is an important indicator of water quality, ecological status, productivity and health of a reservoir, (Janjua *et al.*, (2009). This is due to its importance as a respiratory gas, and its use in biological and chemical reactions. The decrease in dissolved oxygen between block 1 and blocks 2 to 5 could be attributed to waste being discharged into the river by people living along the river. This indicates that most of the discharges are organic in nature and hence required oxygen for decomposition. Generally, these wastes are in the form of soaps and detergents used for washing purposes along the riverside. Lower dissolved oxygen might also be due to higher turbidity and increased suspended materials which affected dissolution of oxygen, (Janjua & Akhtar, 2009). The range of dissolved oxygen recorded of 4.75 mg/l to 8.27 mg/l, shows that the water is of good quality and will promote the growth and survival of fish. Similar observation was recorded during a study on limnology and trophic status of Shahpur dam reservoir, Pakistan (Janjua & Akhtar, 2009). There was significant difference between the levels of dissolved oxygen across all the sampling points according to Student-Newman-Keuls test used at $p< 0.05$ level of significance as shown Appendix 11.

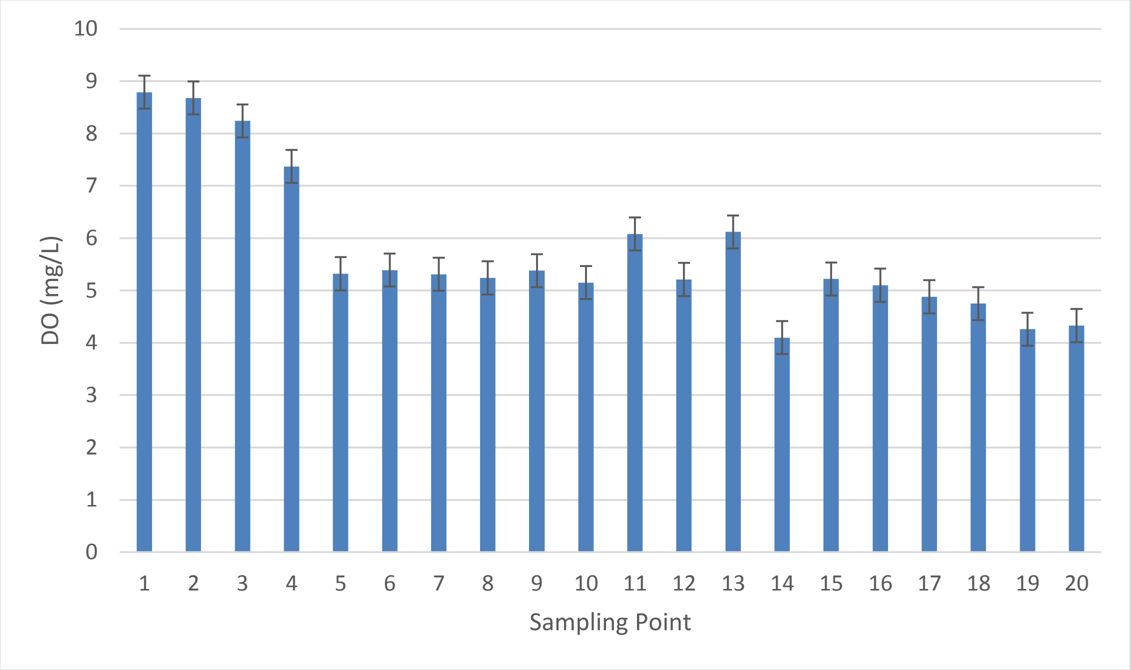

Figure 3.6: **Graph mean concentration of dissolved oxygen**

3.2 Macro-nutrients

3.2.1 Phosphate

Phosphates mean levels ranged from 0.26 ± 0.02 mg/l in sampling point 2 to 0.98 ± 0.02 mg/l in sampling point 20 as shown in Table 3.2 and Figure 3.7. Comparably, these values were below the WHO maximum allowed limits of phosphate in drinking water of 45mg/l. Naturally, phosphates are derived from decomposing organic matter and leaching of phosphorus rich bedrock. Phosphate contamination comes from disposal of detergent contaminated sewage and use of fertilizers and pesticides in farming activities, (Goldman & Horne, 2009). The levels of phosphates in River Mathioya waters were attributed to increasing loading of human wastes, animal wastes, industrial wastes, agricultural activities into the river and the kind of soaps used along the river. Simmilar observation were made during a study on the physico-chemical properties of water of Mouri River, Khulna, Bangladesh, (Goldman & Horne, 2009) and (Kamal et al., 2007). There was significant difference between the levels of phosphates across all the sampling points according to the Student-Newman-Keuls test carried out at $p<0.05$ level of significance as shown in Appendix 12.

Table 3.2: Mean concentration of nitrates, phosphate and fluoride

Sampling point	Number of samples (n)	NO_3(mg/L)	PO_4(mg/L)	F(mg/L)
1.	3	6.23±0.11	0.34 ±0.06	0.67±0.02
2.	3	6.26±0.10	0.26±0.02	0.68±0.02
3.	3	6.56±0.11	0.27±0.02	0.68±0.01
4.	3	6.58±0.11	0.28±0.02	0.68±0.01
5.	3	8.51±0.14	0.32±0.03	0.63±0.01
6.	3	8.43±0.12	0.31±0.03	0.64±0.01
7.	3	8.28±0.14	0.28±0.03	0.90±0.02
8.	3	8.26±0.13	0.69±0.03	0.89±0.01
9.	3	12.71±0.12	0.91±0.02	0.79±0.01
10.	3	12.58±0.15	0.87±0.02	0.80±0.01
11.	3	12.37±0.13	0.85±0.02	0.79±0.01
12.	3	11.80±0.11	0.78±0.02	0.76±0.01

13.	3	13.99±0.11	0.91±0.01	0.91±0.01
14.	3	13.89±0.13	0.89±0.02	0.82±0.01
15.	3	12.83±0.13	0.87±0.01	0.79±0.01
16.	3	14.50±0.15	0.97±0.01	0.87±0.01
17.	3	13.57±0.12	0.97±0.01	0.88±0.01
18.	3	13.28±0.14	0.92±0.01	0.86±0.01
19.	3	12.26±0.16	0.93±0.01	0.91±0.01
20.	3	12.21±0.15	0.98±.02	0.95±.02

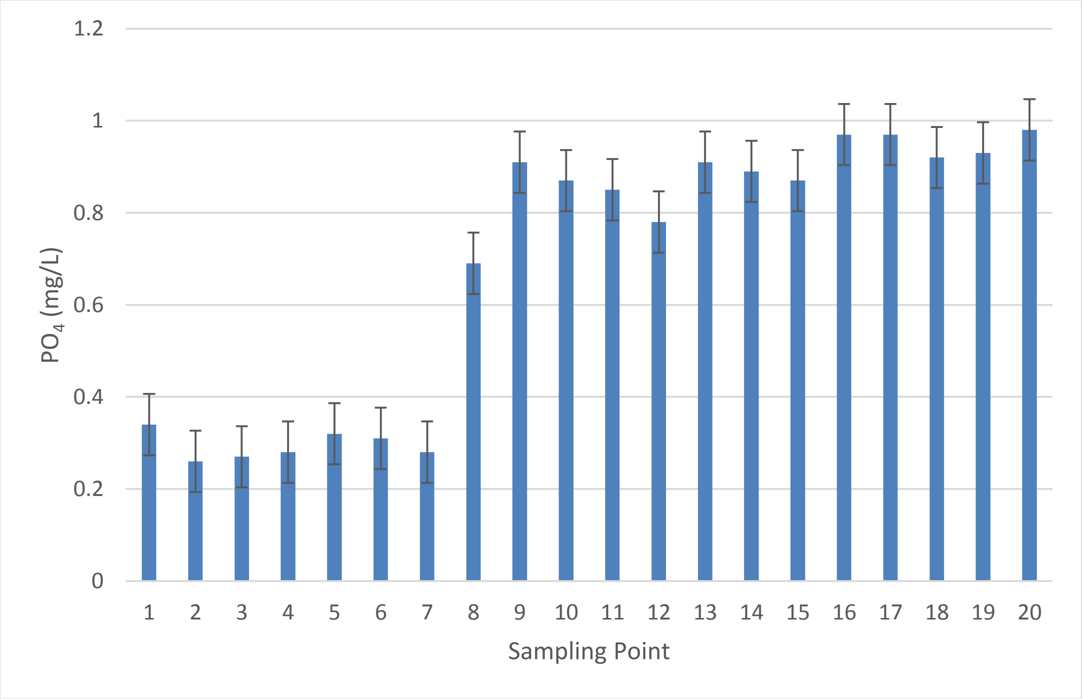

Figure 3.7: Graph of mean concentration of phosphates

3.2.2 Nitrates

Nitrate mean concentration levels ranged from 6.23 ± 0.02 in sampling point 1 to 14.50 ± 0.15mg/L in sampling point 16 as shown in Table 3.2 and Figure 3.8. The values recorded for nitrate were all below the WHO permissible limits of 50 mg/L. Lower levels were obtained by Magut &Terer (2012) during their study on the levels of nitrate ions in water from selected wells and points along Kimondi River, Nandi County, Kenya, which they found to range from 0.18 mg/L to 0.66mg/L. High concentrations of nitrates may give rise to potential health risks such as methemoglobinemia or ‘blue-baby-syndrome’ particularly in pregnant women and bottle-fed infants (Nkansah et al., 2010). The increasing use of artificial fertilizers, the disposal of wastes (particularly from animal farming), and changes in land use are the main factors responsible for the progressive increase in nitrate levels in river water and supplies over the last 20 years (Akinsola, 2005). The nitrates found in the water samples could have come from leaching and run-off from human activities such as agriculture where nitro-phosphate fertilizers are used in the farmlands along the river. Other sources includes domestic effluents and emissions from combustion engines which also reach the river. According to Nolan and Hitt (2006) raw waste effluents from factories and sewage treatment usually have high levels of ammonia and nitrogenous wastes which can lead to rapid multiplication of bacterial population. These can elevate the levels of nitrates in the adjacent water bodies through aerobic and anaerobic bacterial activities. The presence of nitrates in the water samples is suggestive of some bacterial action and bacterial growth (Nolan & Hitt, 2006). There was significant difference between the levels of nitrates across all the sampling points according to the Student-Newman-Keuls test carried out at $p<0.05$ level of significance as shown in Appendix 12.

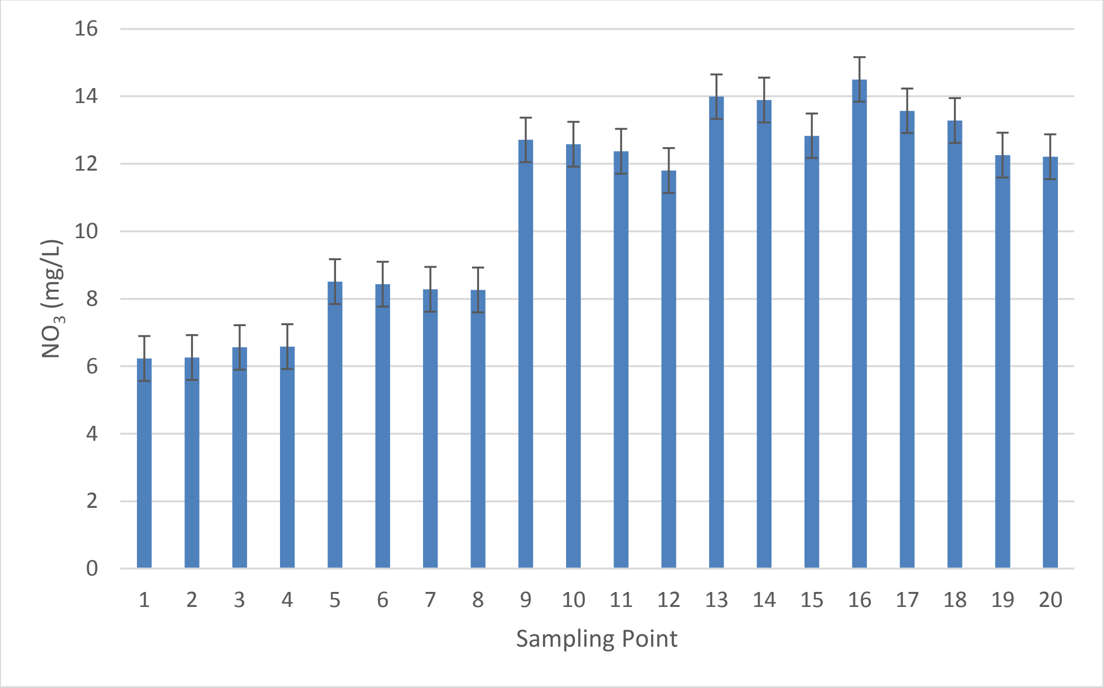

Figure 3.8: Graph of mean concentration of Nitrates

3.2.3 Fluoride

The mean level of fluoride ranged from 0.67 ± 0.02 mg/l in sampling point 1 to 0.95 ± 0.02 mg/l in sampling point 20 as shown in Table 3.2 and Figure 3.9, against the maximum allowed limit of 1.5mg/l. Using Student-Newman-Keuls test as shown in Appendix 12, it was found that there was significant difference between the levels of fluoride across all the sampling points ($p < 0.05$).

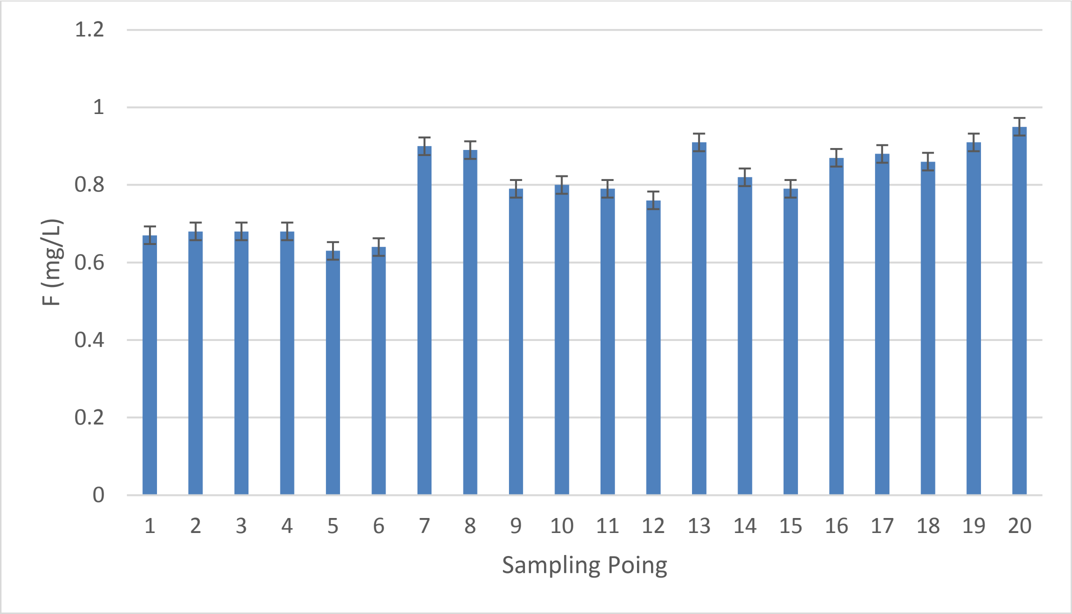

Figure 3.9: **Graph of mean concentration of fluoride**

3.3 Sodium and potassium

3.3.1 Sodium

The mean level of sodium ranged from 73.93 ± 0.72 mg/L to 106.47 ± 0.45 mg/L against the maximum allowed limit of 200mg/L as shown in Table 3.3 and Figure 3.10. Comparably all the values in all the sampling points were below the WHO (2006) maximum allowed limits of sodium in drinking water. There was significant difference between the levels of sodium across all the sapling points at $p<0.05$ level of significance using Student-Newman-Keuls test as shown in Appendix 10. The presence of sodium in the samples might be due to high rate of mineralization in the sediments, increasing sodium into the nutrient pool thereby making more sodium to solubilize. Similar findings from physico-chemical analysis of surface and ground water of Bargarh district, Orissa, India were obtained by Mahananda et al., (2005).

Table 3.3: Mean concentration of sodium and potassium

Sampling point	**Number of samples (n)**	**K(mg/L)**	**Na(mg/L)**
1.	3	3.35 ±0.07	72.98 ±0.39
2.	3	3.36 ±0.12	72.29 ±0.54
3.	3	3.26 ±0.05	71.79 ±0.55
4.	3	3.41 ±0.06	78.63 ±0.43
5.	3	9.17 ±0.19	94.34 ±0.32
6.	3	8.63 ±0.14	96.53 ±0.12
7.	3	8.53 ±0.12	96.10 ±0.68
8.	3	8.46 ±0.16	96.60 ±0.68
9.	3	10.42 ±0.12	99.03 ±0.47
10.	3	9.33 ±0.18	99.13 ±0.22
11.	3	9.37 ±0.08	99.23 ±0.45
12.	3	9.28 ±0.13	97.56 ±0.36
13.	3	10.75 ±0.12	98.78 ±0.21
14.	3	11.03 ±0.14	97.47 ±0.47
15.	3	6.25 ±0.13	98.35 ±0.45
16.	3	6.15 ±0.11	98.09 ±0.44
17.	3	9.33 ±0.18	101.07 ±0.22
18.	3	18.41 ±0.46	102.14 ±0.12
19.	3	17.42 ±0.15	99.29 ±0.14
20.	3	17.54 ±0.29	100.07 ±0.22

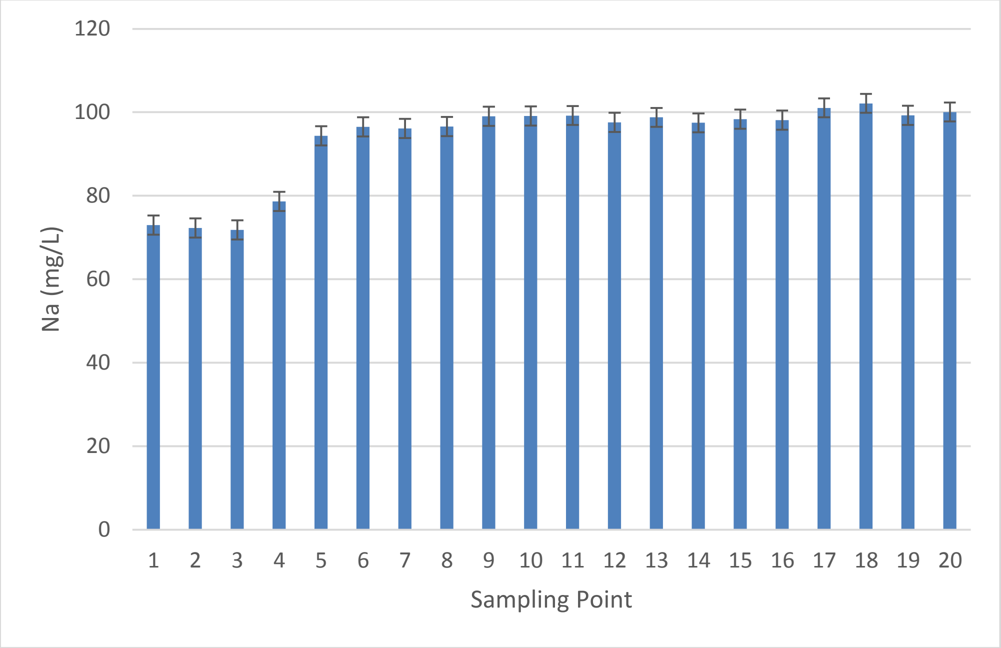

Figure 3.10: **Graph of mean concentration of sodium**

3.3.2 Potasium

The mean level of potassium ranged from 3.35 ± 0.07 mg/L in sampling point 1 to 18.41± 0.46 sampling point 18 mg/L as shown in Table 3.3 and Figure 3.11. Similar results were observed similar findings from their study on physico-chemical analysis of surface and ground water of Bargarh district, Orissa, India. There was significant difference between the levels of potassium across all the sampling point ($p < 0.05$) using Student-Newman-Keuls test as shown in Appendix 10.

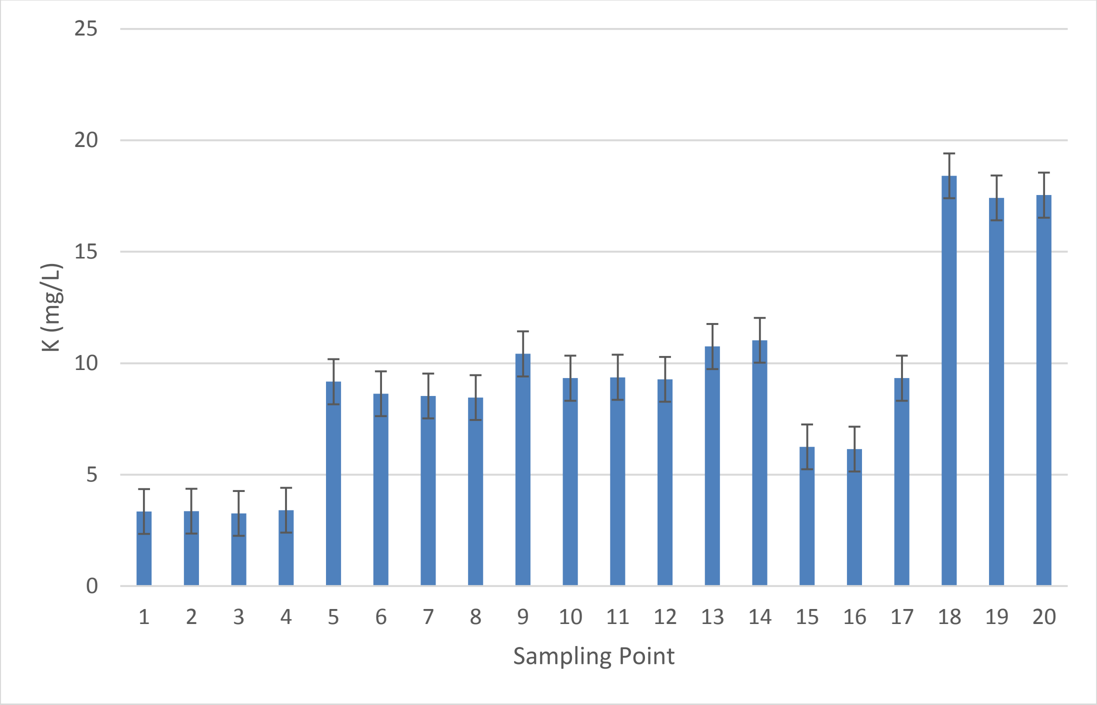

Figure 3.11: **Graph of mean concentration of potassium**

3.4 Heavy metals

3.4.1 Iron

The mean level of iron ranged from 0.70 ± 0.02 mg/L sampling point to 1.89± 0.08 mg/L sampling point 15 as shown in Table 3.4 and Figure 3.12. Comparably, these values were high1er than the WHO (2006) maximum allowed limits of 0.5 mg/L in drinking water. The presence of iron in water samples analyzed could be attributed to inflows from garages metal works and commercial establishments in the upstream, sewage waste discharge into Karii stream, car wash sheds and natural deposits. Physicochemical and bacteriological characteristics of water samples from Irigu River, Meru County, Kenya, were investigated and the results showed that the iron content was higher than the WHO acceptable limits in drinking water (Ombaka & Gichumbi, 2012). There was significant difference between the levels of iron across all the sampling points ($p < 0.05$) according to Student-Newman-Keuls test used for the data obtained as shown in Appendix 9.

Table 3.4: Mean concentration of heavy metals

Sampling point	Number of samples (n)	Fe(mg/L)	Mn(mg/L)	Zn(mg/L)	Cu(mg/L)	Pb(mg/L)	Cr(mg/L)
1	3	0.70 ±0.02	0.88 ±0.02	0.04 ±0.01	0.03 ±0.01	LOD	0.03 ±0.01
2	3	0.75 ±0.03	0.92 ±0.04	0.05 ±0.01	0.03 ±0.01	LOD	0.02 ±0.01
3	3	0.71 ±0.02	0.89 ±0.03	0.06 ±0.01	0.03 ±0.01	LOD	0.02 ±0.01
4	3	0.75 ±0.02	0.81 ±0.04	0.04 ±0.02	0.03 ±0.01	LOD	0.03 ±0.01
5	3	0.89 ±0.02	0.95 ±0.04	0.07 ±0.02	0.03 ±0.01	LOD	0.03 ±0.01
6	3	0.85 ±0.04	0.93 ±0.03	0.07 ±0.01	0.03±0.01	LOD	0.03 ±0.01
7	3	0.75 ±0.02	0.89 ±0.02	0.05 ±0.02	0.03 ±0.01	LOD	0.04 ±0.01
8	3	0.75 ±0.05	0.89 ±0.01	0.07 ±0.02	0.03 ±0.01	LOD	0.03 ±0.01
9	3	0.87 ±0.03	2.37 ±0.04	0.08 ±0.01	0.03 ±0.01	LOD	0.03 ±0.01
10	3	0.87 ±0.03	2.25 ±0.04	0.08 ±0.01	0.03 ±0.01	LOD	0.03 ±0.01
11	3	0.83 ±0.03	2.24 ±0.05	0.08 ±0.01	0.02 ±0.01	LOD	0.03 ±0.01
12	3	0.77 ±0.04	2.10 ±0.02	0.08 ±0.02	0.02 ±0.01	LOD	0.03 ±0.01
13	3	1.14 ±0.04	1.13 ±0.04	0.07 ±0.02	0.03 ±0.01	LOD	0.03 ±0.01
14	3	1.38 ±0.04	1.74 ±0.02	0.79 ±0.02	0.03 ±0.01	LOD	0.03 ±0.01
15	3	1.89 ±0.08	1.18 ±0.04	0.07 ±0.02	0.04 ±0.01	LOD	0.03 ±0.01
16	3	1.76 ±0.05	0.88 ±0.02	0.07 ±0.02	0.03 ±0.01	LOD	0.03 ±0.01
17	3	0.87 ±0.01	2.25 ±0.04	0.08 ±0.01	0.03 ±0.01	LOD	0.03 ±0.01
18	3	1.57 ±0.05	4.19 ±0.04	0.08±0.01	0.03 ±0.01	LOD	0.03 ±0.01
19	3	1.11 ±0.04	1.18 ±0.02	0.08 ±0.01	0.03 ±0.01	LOD	0.03 ±0.01
20	3	1.13 ±0.03	1.18 ±0.01	0.07 ±0.02	0.03 ±0.01	LOD	0.03 ±0.01

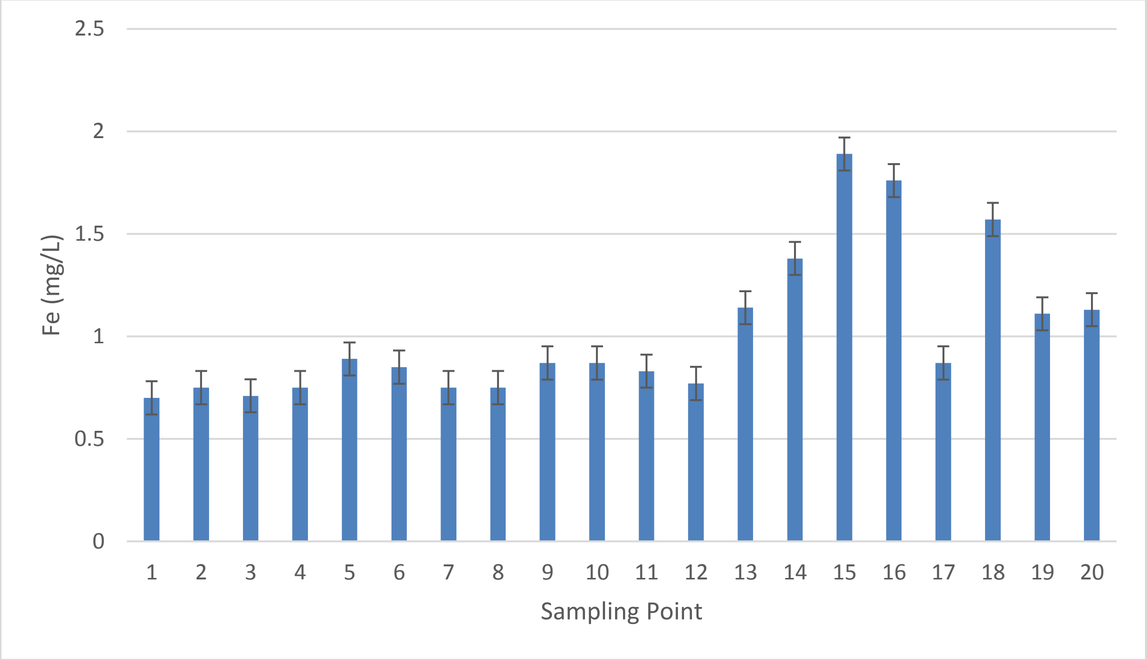

Figure 3.12: **Graph of mean concentration of iron**

3.4.2 Manganese

The mean levels ranged from 0.88 ± 0.02 mg/l in sampling point 1 to 4.19 ± 0.10 mg/l in sampling point 18 as shown in Table 3.4 and Figure 3.13. Comparably, these values were higher than the WHO (2005) maximum allowed limits of limit of 0.1 mg/l manganese in drinking water. The presence of manganese in water samples could be attributed to vehicular emission and inflows from garages metal works and commercial establishments in the town, sewage, wastewater from town effluents, petrol stations, carwash sheds and paints from garages, waste batteries, and plastics. Similarly in their study, Wogu and Okaka (2011) recorded values of manganese in river water ranging from 0.020-0.680 mg/l. Charcoal burning and wastes especially from batteries are known to be a major source of Manganese. Similar study from Athi-Galana-Sabaki tributaries, Kenya, showed that the concentrations of lead, manganese and chromium in water were more than the WHO recommended limit thus posing immediate fears of bioaccumulation in man **(**Muiruri, & Nawiri, 2013). Using Student-Newman-Keuls test, it was found that there was significant difference between the levels of manganese across all the sampling points ($p < 0.05$) according to Student-Newman-Keuls test used for the data obtained as shown in Appendix 10.

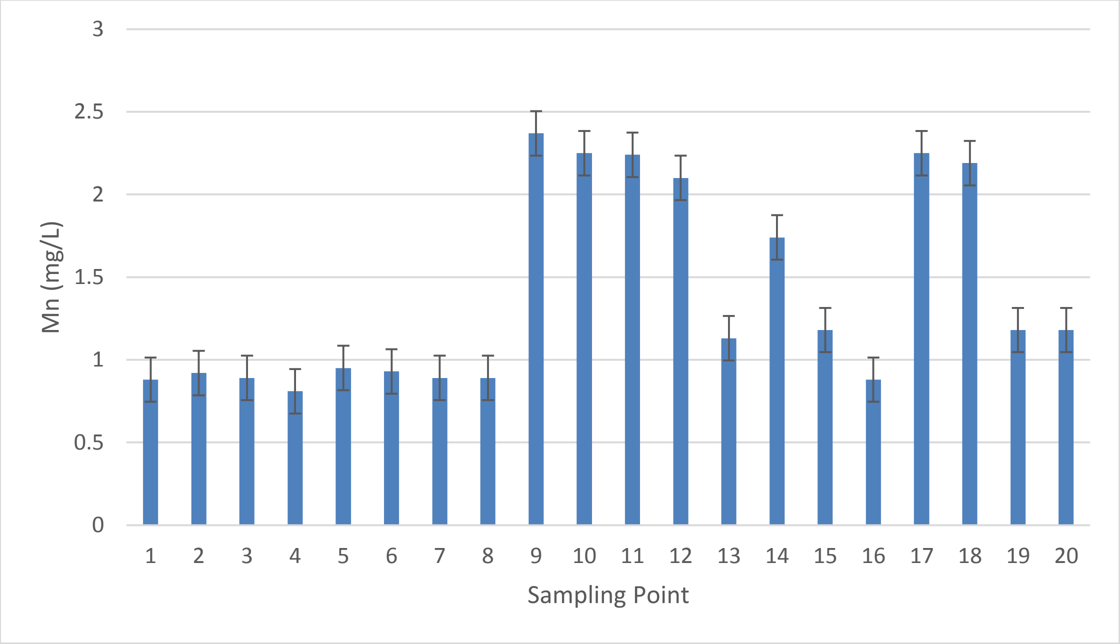

Figure 3.13: Graph of mean concentration of manganese

3.4.3 Zinc

The mean levels of zinc ranged from 0.04 ±0.01 in sampling point 1 mg/L to 0.08 ± 0.01 mg/L in sampling point 9 as shown in Table 3.4 and Figure 3.14. Comparably, all the mean values of zinc obtained in all the blocks were lower than the WHO (2005) maximum allowed limits of 3.0 mg/l in drinking water. There was no significant difference between the levels of zinc across all the sampling points ($p < 0.05$) according to Student-Newman-Keuls test(0.103) as shown in Appendix 9. The presence of zinc in Mathioya River water samples, might be due to agricultural run-off on sediments in the river, carrying various zinc based pesticides used in agricultural practices. This largely agrees with findings recorded during a study on heavy metals (Cu and Zn) in sediments of Ilangrose Lake (Muiruri & Nawiri, 2013).

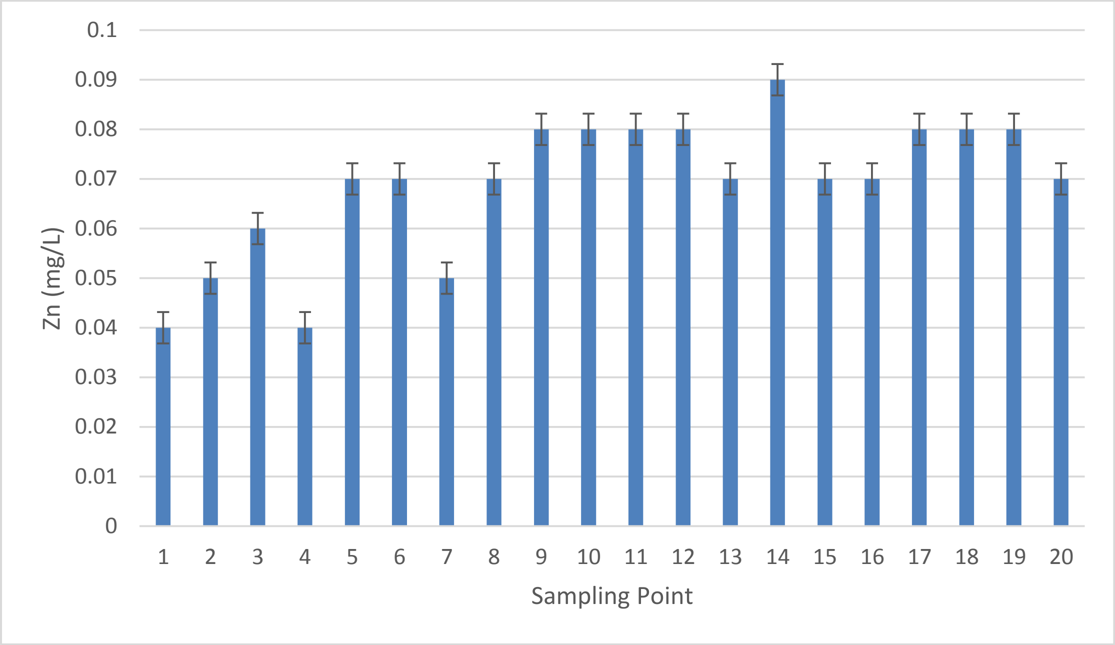

Figure 3.14: **Graph of mean concentration of zinc**

3.4.4 Copper

The levels of copper ranged from 0.02 ± 0.01 mg/l in sampling point 1 to 0.04 ± 0.02 mg/L in sampling point 15 as shown in Table 3.4 and Figure 3.15. Comparably, the mean concentration values of copper in all the blocks were below the allowed limit of 1 mg/L by the WHO (2005). There was no significant difference between the mean levels of copper in all the sampling points ($p < 0.05$) as shown by Student-Newman-Keuls test(1.00) in Appendix 9. Presence of copper in the water samples was attributed to corrosion of copper containing alloys in the pipe fittings in Muranga town. Copper may occur in natural waters, waste waters and industrial waters as soluble salts and precipitated copper compounds (Callatay and Francois, 2005). During a study in Cairo, Egypt, to determine heavy metals (e.g. copper, lead, and chromium) in drinking water and their environmental impact on human health, a relationship between chronic diseases and the geological environment was found (Hanaa & Azza, 2000).

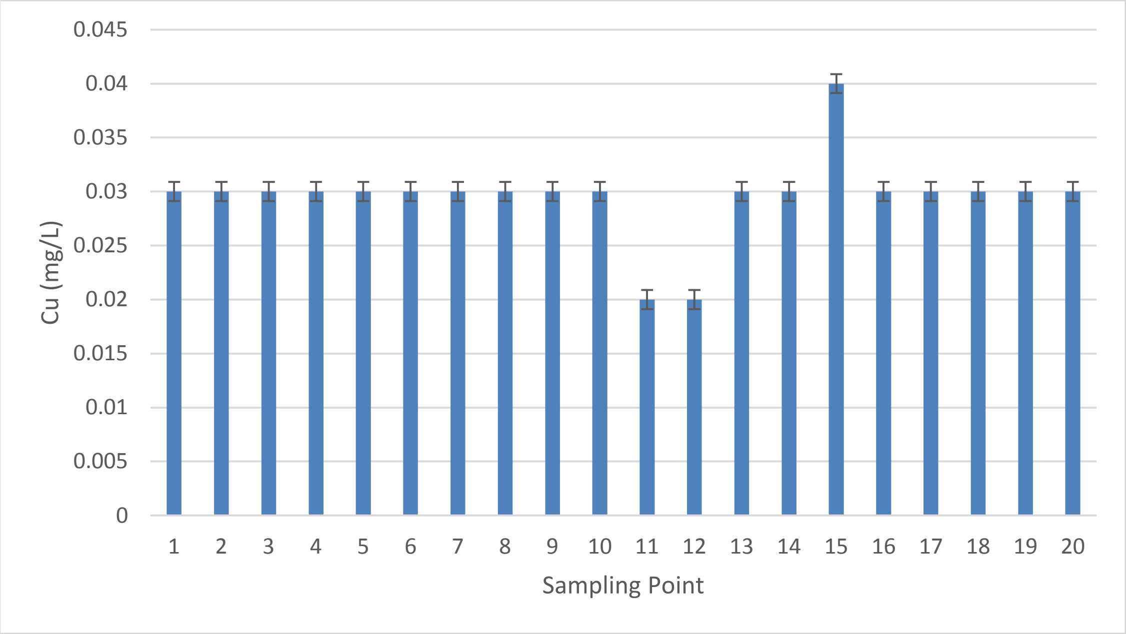

Figure 3.15: **Graph of mean concentration of copper**

3.4.5 Lead

The mean levels of lead in all the five sampling blocks were below the limit of detection (LOD) as shown in Table 3.4. This means that the level of lead are below the maximum WHO limits of 0.05 mg/l of lead in drinking water. The sources of lead into rivers could include sewage, paints from garages and buildings, old automobiles and fertilizers. Lead is the most significant of all the heavy metals because it is toxic, very common and harmful even in small amounts (Mebrahtu & Zerabruk, 2011). Lead enters the human body in many ways, it can be inhaled in dust from lead paints, or waste gases from leaded gasoline. It is found in trace amounts in various foods, notably in fish, which are heavily subjected to industrial pollution. Most of the lead we take is removed from our bodies in urine; however, as exposure to lead is cumulative over time, there is still risk of buildup, particularly in children. Studies on lead are numerous because of its hazardous effects. High concentration of lead in the body can cause death or permanent damage to the central nervous system, the brain, and kidneys (Mebrahtu & Zerabruk, 2011). There was no significant difference between all the levels of lead across all the sampling points at ($p < 0.05$), according to Student-Newman-Keuls test($p= 0.466$) used for the data analysis as shown in Appendix 9.

3.4.6 Chromium

The mean levels of chromium ranged from 0.02 ± 0.01 mg/l in sampling point 3 to 0.03 ± 0.01 mg/l in sampling point 1 as shown in Table 3.4 and Figure 3.16 against allowed limit of 0.050 mg/L chromium in drinking water. Similar results were obtained by Wogu and Okaka (2011) in a study on surface water of Warri River, Nigeria, where lower levels of chromium ranging from 0.0 mg/l to 0.06 mg/L were recorded. The presence of chromium in the water samples could be attributed to sources such as cement, dyes, paints, printing ink, detergents, wood preservatives among others (Hilgenkamp, 2006), which are common in Murang'a town and its environs. Excess of pesticides and fertilizers which are not used by plants will percolate into the soil with the rain water and consequently, reach the river water wherever the permeability of the soil permits. Uses of large amounts of phosphate fertilizers in agriculture and many types of pesticides may also led to the relatively high concentrations of chromium in water. Disposal of plastics and batteries may also be considered a source of chromium in water (Mandour & Azab, 2011).There was no significant difference between the levels of chromium across all the sampling points at ($p < 0.05$), according to Student-Newman-Keuls test(1.00) used for the data obtained in Appendix 9.

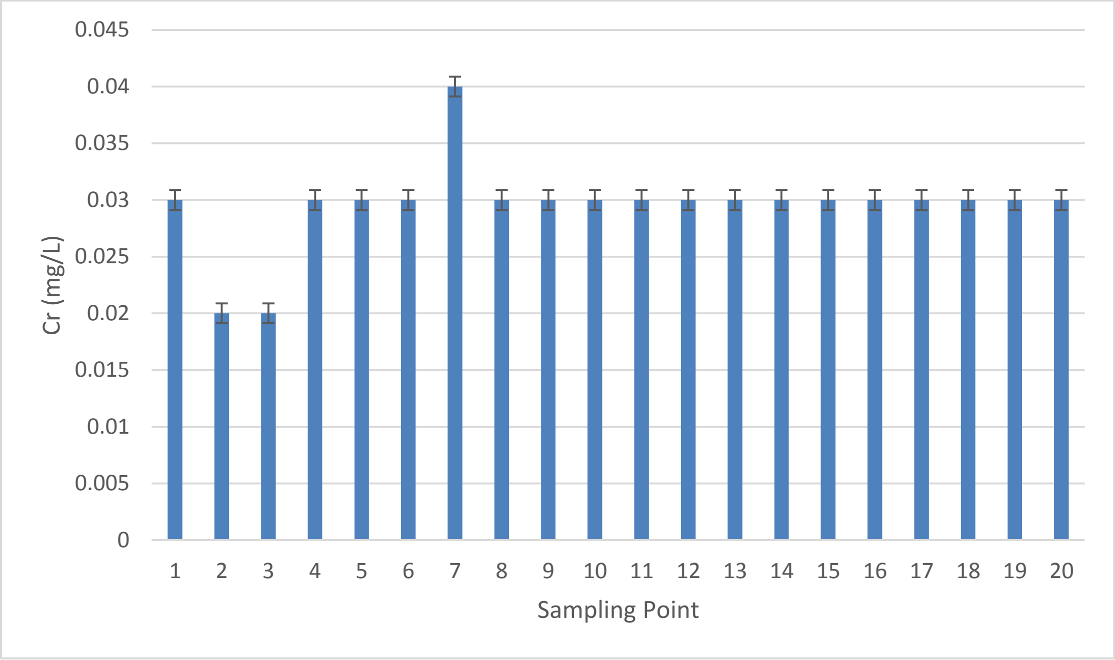

Figure 3.16: Graph of mean concentration of chromium

CHAPTER FOUR

CONCLUSION AND RECOMMENDATIONS

4.1 Conclusion

The mean levels of physico-chemical parameters pH (6.94 to 7.76), TDS (37.84 to 54.59 mg/L), TSS (42.78 to 53.84 mg/L), DO (4.75 to 8.27 mg/L) and EC (63.89 to 80.17µS/cm) were all within the acceptable guidelines on drinking water by the WHO (2005). In this study, the concentrations of the investigated nutrients, nitrates (6.40 - 13.66 mg/L) and phosphates (0.29 – 0.91 mg/L) in the water samples were found to be within the acceptable limits according to the guidelines for raw drinking water provided by the WHO (2005). The levels of fluoride (0.68 – 0.88 mg/L) were found to be lower than WHO value of 1.5 mg/L allowed in drinking water in all the sampling points. The level of sodium and potassium mean concentration was found to be lower than WHO value in all the sampling points. The study showed that except for lead which was not detected, there was considerable amount of heavy metals in the water samples of Mathioya River, were below the maximum permissible WHO limits (zinc 0.05 - 0.08 mg/L), chromium (0.02 - 0.03 mg/L), lead below LOD and copper (0.03 - 0.04 mg/L) while levels of iron (0.73 - 1.16 mg/L) and manganese (0.88- 2.24 mg/L) exceeded permissible limits. The water samples from blocks 4 (Murari stream) and 5 (Karii stream) were more polluted with heavy metals than block 1 which was used as a control (upstream before town). Blocks 2 and 3 also had higher mean concentrations of heavy metals than block 1, which could be attributed to discharges from blocks 4 and 5, but their concentrations were lower than for blocks 4 and 5 because of dilution by Mathioya River water. The study has revealed that Muranga town effluents contribute to the pollution of River Mathioya since the mean concentrations for the studied parameters are higher in blocks 2-5 that receive effluents from Muranga town than block 1 which is upstream of the town.

4.2 Recommendations

1. There is an urgent need to properly manage wastes from the Muranga town and control and monitor human activities in order to ensure minimized effects of these effluents on the water of River Mathioya.
2. From the study, it is recommended that there should be appropriate education on the proper handling, use and disposal of agrochemicals such as fertilizers.
3. There should be proper planning of vehicle repairs and maintenance sheds and good location of car washing areas.
4. Necessary protective and conservation measures of the river should be implemented.
5. Water treatment should aim at lowering the iron and manganese to the accepted levels in drinking water.
6. Research should be carried out in the rivers sediments and plants that have grown along the river to determine whether similar levels of the studied parameters and other heavy metals are present.
7. The Muranga County government should treat the sewage waste before discharging into Karii stream.

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APPENDICES

Appendix 1: Calibration curve for sodium

Working condition

Method: flame emission

Fuel: acetylene

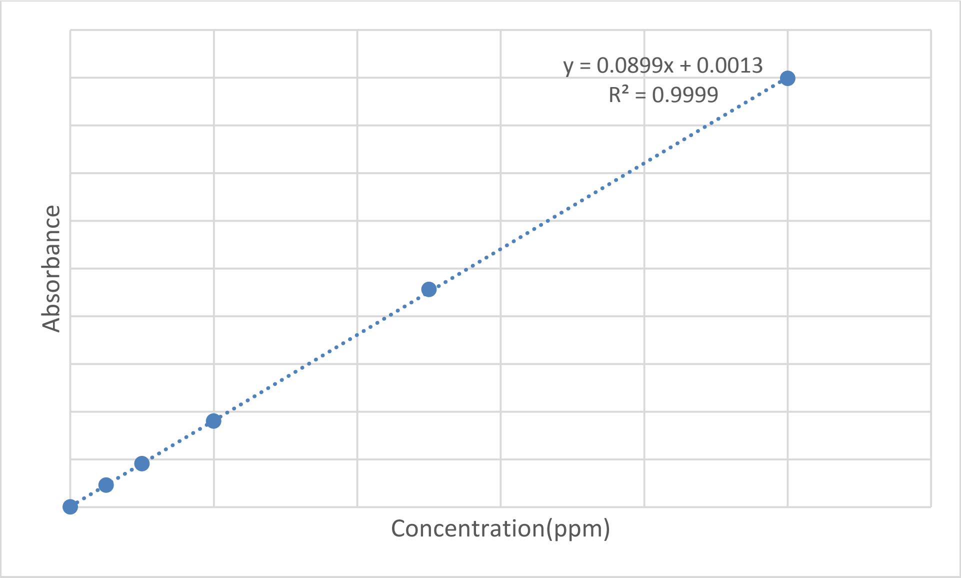
Support/oxidant: Air

Wavelength: 589.0nm

Slit width: 0.1nm

Detection limit: 0.0003 ppm.

S/No	**Abs**	**Concentration**
1	0.000	0.00
2	0.046	0.50
3	0.091	1.00
4	0.18	2.00
5	0.456	5.00
6	0.898	10.00



Appendix 2: Calibration curve for potassium

Working condition

Method: flame emission

Fuel: acetylene

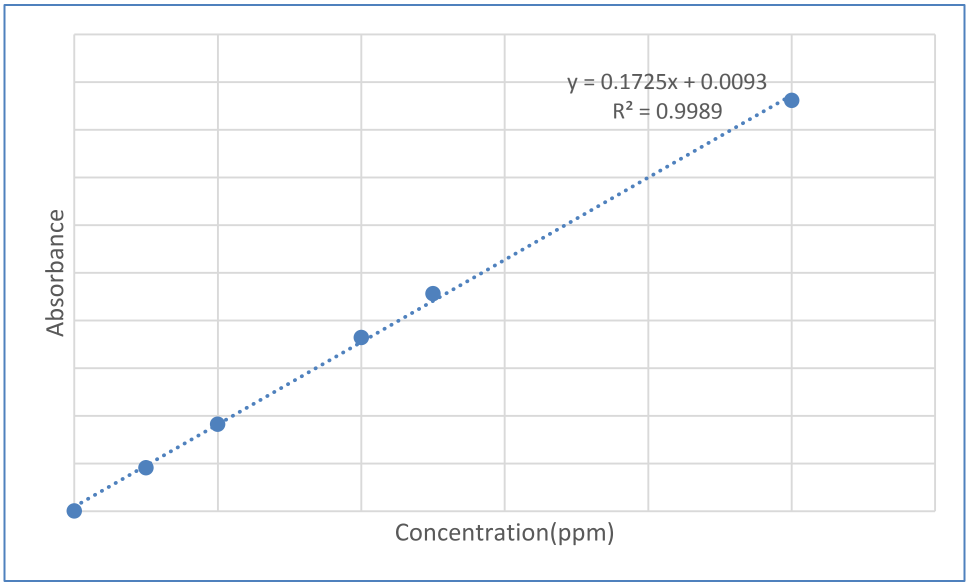
Support/oxidant: Air

Wavelength: 766.5nm

Slit width: 0.1nm

Detection limit: 0.0003 ppm.

S/No	**Abs**	**Concentration**
1	0.000	0.00
2	0.091	0.50
3	0.182	1.00
4	0.364	2.00
5	0.456	2.50
6	0.861	5.00

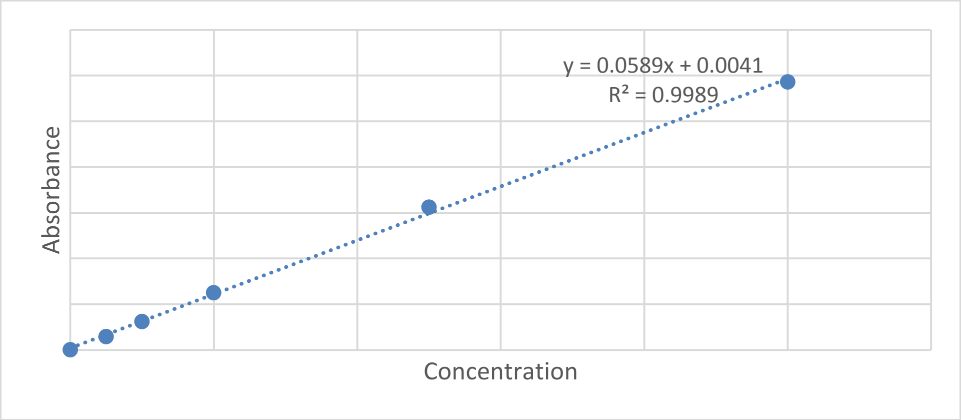


Appendix 3: Calibration curve for iron

Working condition

Method:	atomic absorption
Lamp current:	8 mA
Fuel:	acetylene
Support/oxidant:	Air
Wavelength:	248.3 nm
Slit width:	0.2nm
Detection limit:	0.005 ppm.

S/No	Abs	Concentration
1	0.000	0.00
2	0.029	0.50
3	0.062	1.00
4	0.125	2.00
5	0.312	5.00
6	0.586	10.00

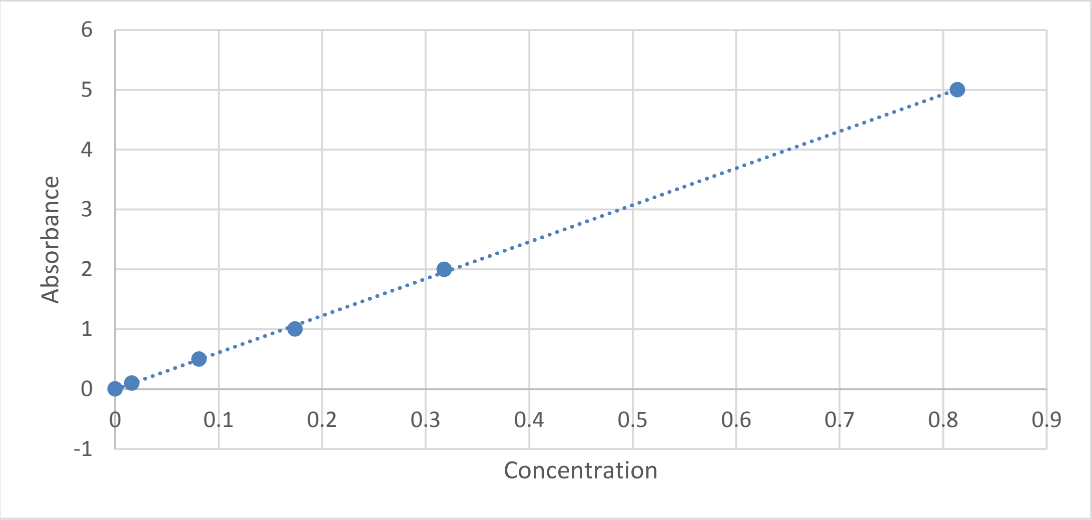


Appendix 4: Calibration curve for manganese

Working condition

Method:	atomic absorption
Lamp current:	5mA
Fuel:	Acetylene
Support/oxidant:	Air
Wavelength:	279.5nm
Slit width:	0.2nm
Detection limit:	0.003 ppm.

S/No	Abs	Concentration
1	0.000	0.00
2	0.016	0.100
3	0.081	0.500
4	0.174	1.000
5	0.318	2.000
6	0.814	5.000



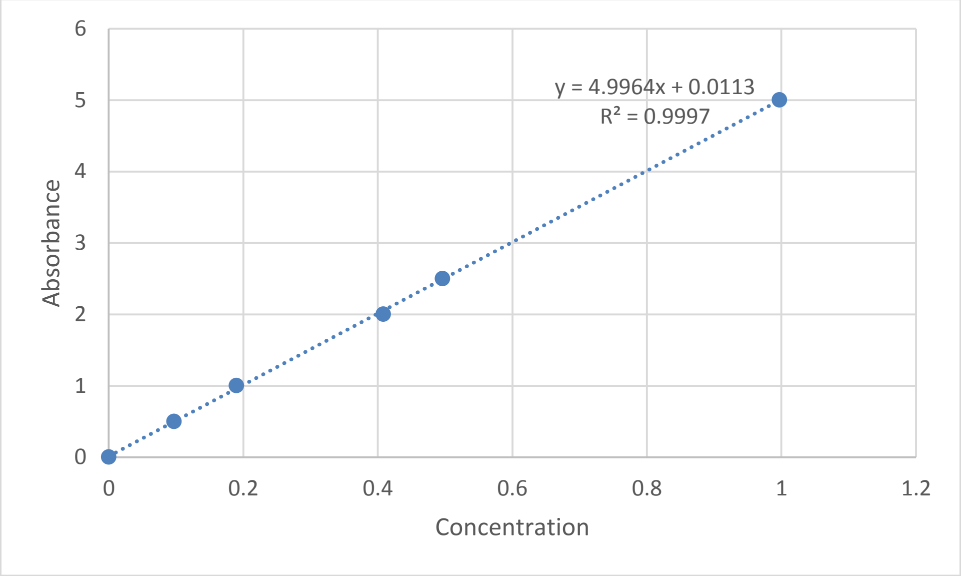
Appendix 5: Calibration curve for zinc

Working condition

Method:	atomic absorption
Lamp current:	5mA
Fuel:	Acetylene
Support/oxidant:	Air
Wavelength:	213.9 nm
Slit width:	1.0nm
Detection limit:	0.002 ppm.

S/No	Abs	Concentration
1	0.000	0.00
2	0.097	0.500
3	0.190	1.000
4	0.408	2.000
5	0.496	2.500

6	0.997	5.000



Appendix 6: Calibration curve for copper

Working condition

Method: atomic absorption

Lamp current: 3mA

Fuel: Acetylene

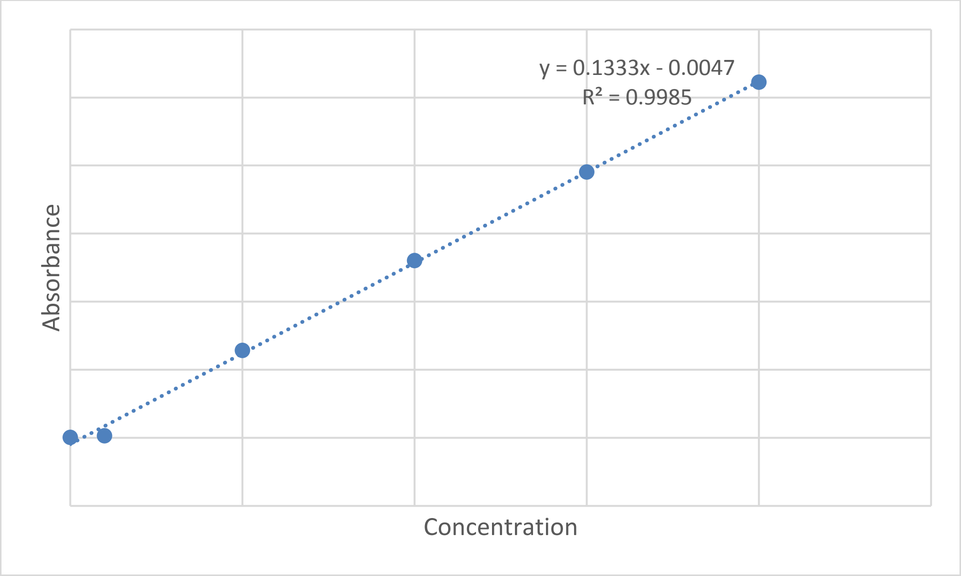
Support/oxidant: Air

Wavelength: 324.7 nm

Slit width: 0.5nm

Detection limit: 0.003 ppm.

S/No	Abs	Concentration
1.	0.000	0.00
2.	0.064	0.50
3.	0.130	1.00
4.	0.195	1.50
5.	0.261	2.00



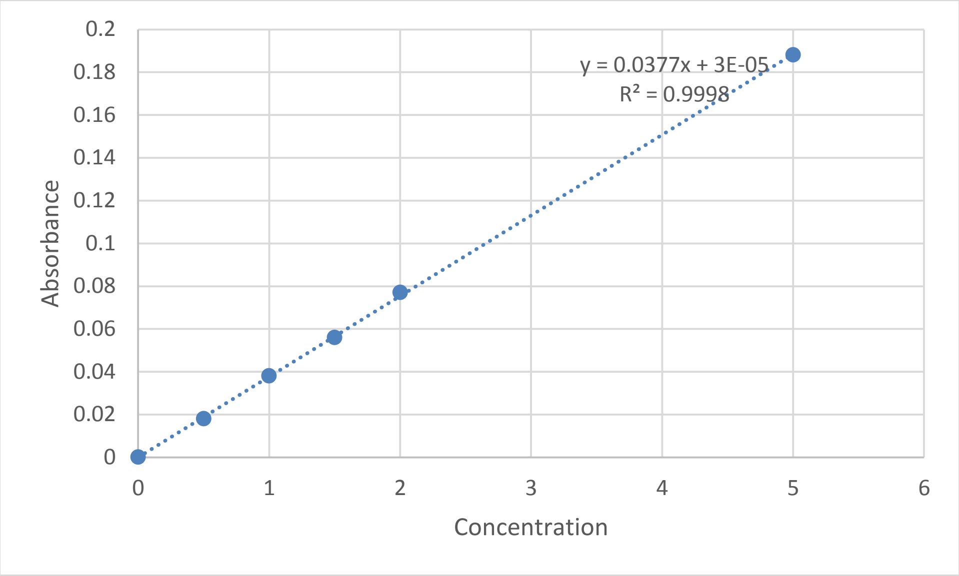
Appendix 7: Calibration curve for lead

Working condition

Method:	atomic absorption
Lamp current:	8mA
Fuel:	Acetylene
Support/oxidant:	Air
Wavelength:	217.0nm
Slit width:	1.0nm
Detection limit:	0.02 ppm.

S/No	Abs	Concentration
1	0.000	0.00
2	0.018	0.500
3	0.038	1.000
4	0.056	1.500

5	0.077	2.000
6	0.188	5.000



Appendix 8: Calibration curve for chromium

Working condition

Method: atomic absorption

Lamp current: 7mA

Fuel: Acetylene

Support/oxidant: Nitrous acid

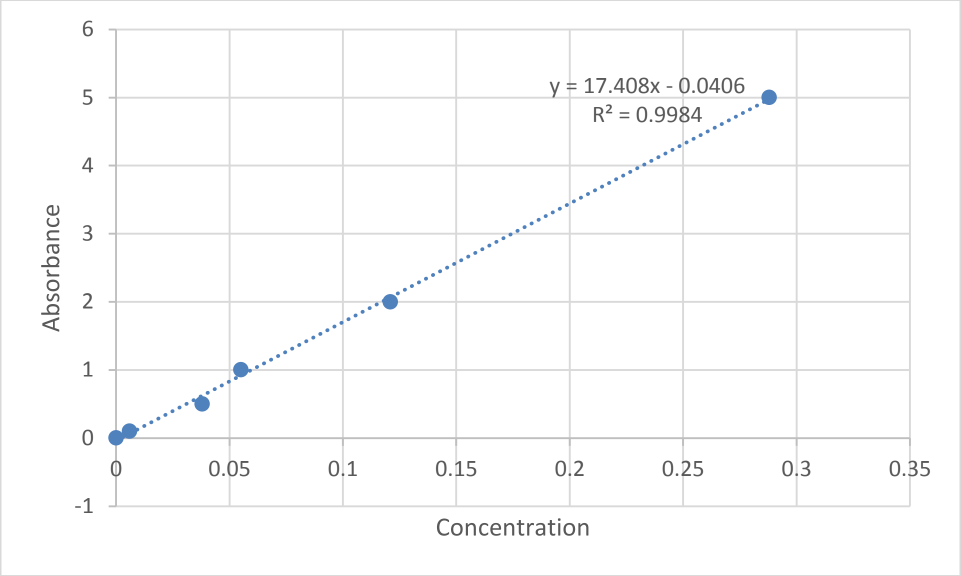
Wavelength: 357.7 nm

Slit width: 0.2nm

Detection limit: 0.005 ppm.

s/no	Abs	Concentration
1	0.000	0.00
2	0.006	0.100
3	0.038	0.500

4	0.055	1.000
5	0.121	2.000
6	0.288	5.000



Appendix 9: Anova table for heavy metals

		Sum of Squares	df	Mean Square	F	Sig.
Iron * sampling points	Between Groups	7.349	19	.387	159.232	.000
	Within Groups	.097	40	.002		
	Total	7.447	59			
Manganese * sampling points	Between Groups	41.448	19	2.181	1.375	.000
	Within Groups	.063	40	.002		
	Total	41.511	59			
Zinc * sampling points	Between Groups	.011	19	.001	1.606	.103
	Within Groups	.014	40	.000		

	Total	.024	59			
Copper * sampling points	Between Groups	.001	19	.000	.137	1.000
	Within Groups	.009	40	.000		
	Total	.009	59			
Lead * sampling points	Between Groups	.001	19	.000	1.015	.466
	Within Groups	.002	40	.000		
	Total	.003	59			
Chromium * sampling points	Between Groups	.001	19	.000	.153	1.000
	Within Groups	.007	40	.000		
	Total	.008	59			

Appendix 10: Anova table for Sodium and potassium

						Sig.
Potassium * sampling points	Between Groups	1361.125	19	71.638	1.601	.000
	Within Groups	1.790	40	.045		
	Total	1362.915	59			
Sodium* sampling points	Between Groups	287.783	19	15.146	24.434	.000
	Within Groups	24.795	40	.620		
	Total	312.579	59			

Appendix 11: Anova table for physico-chemical parameters

						Sig.
Temp * sampling points	Between Groups	177.525	19	9.343	21.409	.000
	Within Groups	17.457	40	.436		
	Total	194.982	59			
DO * sampling points	Between Groups	114.422	19	6.022	265.463	.000
	Within Groups	.907	40	.023		
	Total	115.330	59			
pH * sampling points	Between Groups	6.571	19	.346	22.854	.000
	Within Groups	.605	40	.015		
	Total	7.177	59			
TDS * sampling points	Between Groups	2528.486	19	133.078	43.958	.000
	Within Groups	121.095	40	3.027		

	Total	2649.580	59			
TSS * sampling points	Between Groups	1196.311	19	62.964	81.869	.000
	Within Groups	30.763	40	.769		
	Total	1227.075	59			
EC * sampling points	Between Groups	2846.962	19	149.840	3.400	.000
	Within Groups	1.763	40	.044		
	Total	2848.725	59			

Appendix 12: Anova table for macronutrients

						Sig.
Nitrates * sampling points	Between Groups	523.665	19	27.561	1.070	.000
	Within Groups	1.031	40	.026		
	Total	524.696	59			
Phosphates * sampling points	Between Groups	5.024	19	.264	328.472	.000
	Within Groups	.032	40	.001		
	Total	5.056	59			
Flouride * sampling points	Between Groups	.513	19	.027	122.843	.000
	Within Groups	.009	40	.000		
	Total	.522	59			