ASSESSMENT OF HEAVY METAL CONTAMINATION IN WATER, SOIL AND VEGETABLES IN TWO URBAN STREAMS IN MACHAKOS MUNICIPALITY, KENYA.

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DECLARATION

This thesis is my original work and has not been presented for the award of a degree in any other university or any other award.

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DEDICATION

I dedicate this thesis to my beloved husband, my sons; Ian and Jay, daughter Amy, my dear parents and all my friends all who continually provide their moral, emotional and spiritual support.

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LIST OF ABBREVIATIONS

ANOVA	One-way Analysis of Variance
BDL	Below detectable limit
Cd	Cadmium
CMS	Carboxymethyl starch
Cr	Chromium
Cu	Copper
EC	Electrical Conductivity
EU	European Union
GOK	Government of Kenya
GPS	Global positioning system
HDL	High-density lipoprotein
IQ	Intelligence Quotient
ICP-MS	Inductively Coupled Mass Spectrometer
LDL	Low-density lipoprotein
KEPHIS	Kenya Plant Health Inspectorate Service
NEMA	National Environmental Management Authority
NIST	National Institute of Standards and Technology

OAM	Open-air market
Pb	Lead
PEI	Polyethylenimine
ppb	Parts per billion
ppm	Parts per million
PSU	Polymer supported ultra-filtration
PVCs	Polyvinyl chlorides
RDA	Recommended dietary allowances
SPM	Supermarket
SRM	Standard Reference Material
TDS	Total Dissolved Solids
TF	Transfer factor
USEPA	United States Environmental Protection Agency
UF	Ultra-filtration
WHO	World Health Organization
Zn	Zinc

ABSTRACT

Presence of heavy metals in our environment is of great concern since the heavy metals bio-accumulate in food chains posing harmful health effects to humans who are consumers of food grown in such environments. This study sought to determine the concentration of selected heavy metals (Cd, Pb, Cr, Zn and Cu) in urban stream water, soil and vegetables (spinach and kale) in Machakos municipality. Water and soil samples were collected along the rivers under study. Vegetables (spinach and kale) grown along the rivers, as well as vegetables sold in the market sites in the municipality were also collected for analysis. All the collected samples were analyzed for heavy metal concentrations using the inductively coupled plasma mass spectrometer (ICP-MS). Before heavy metal analysis, the vegetable and soil samples were oven dried, ground and digested using a tri acid mixture (HNO_3, $HClO_4$ and HCl). The water samples were also digested in a tri acid mixture prior to heavy metal analysis. Physico-chemical parameters for the river water (temperature, pH, total dissolved solids (TDS) and electrical conductivity (EC)) were measured on-site using standard portable meters. The data was analyzed using the Minitab Statistical software, version 19. One -way Analysis of variance (ANOVA) was used to test for the significant difference ($p \leq 0.05$) of heavy metal concentrations in vegetables, soil, and water among the different sampling sites. Heavy metal concentrations were compared with acceptable standards by the World Health Organization (WHO) for irrigation water, agricultural soil and vegetables for human consumption. Carboxymethyl starch was synthesized and its ability to remove heavy metals from water through chelation determined. The mean levels of the Physico-chemical parameters ranged from 7.5 – 8.45 pH, 21.58 – 23.05 ºC temperature, 577.5 – 865.83 mg/L total dissolved solids (TDS) and 864.83 – 1778.5 µs/cm electrical conductivity (EC). Mean values of pH were observed to be significantly different ($p = 0.000$) among the sampling sites. Temperature, pH and TDS were within the WHO recommended limit for surface water while EC values exceeded the World Health Organization (WHO) set limit. The mean concentrations (mg/L) for heavy metals in water were found to be; Cd (0.0005 – 0.0011), Cu (0.0034 – 0.0055), Pb (0.0012 – 0.007), Zn (0.0232 – 0.1351) and Cr (0.0036 – 0.0292), while mean values (mg/kg) in soil were; Cd (0.0058 – 0.0534), Cu (10.39 – 27.5), Pb (4.23 – 8.35), Zn (20.1 – 28.80) and Cr (8.17 – 10.03). Mean concentration values (mg/kg) for the heavy metals in vegetables were; Cd (0.004 – 0.243), Cu (0.909 – 14.5), Zn (9.05 – 26.7), Pb (0.098 – 0.0.867) and Cr (0.112 – 14.0). The levels of heavy metals in water and soil were found to be within the WHO acceptable standards. The mean concentration of Pb, Zn and Cr in vegetables from some of the sampling sites exceeded WHO acceptable levels. Pearson correlation matrix showed positive correlations between heavy metals concentrations in soil, water and vegetables. Carboxymethyl starch was found to chelate heavy metals to a greater percentage; 92.31% Cd, 66.90% Pb, 66.19% Zn, 66.18% Cu and 14.37% Cr, thus a potential material for remediation of heavy metals in water. Presence of heavy metals (Zn, Pb, and Cr) in spinach and kales signifies a health hazard from consumption of these vegetables. This study thus recommends proper treatment and disposal of effluent based on best practices and continuous monitoring of heavy metals in urban stream water, soil and vegetables as it is critical towards safe guarding public health.

CHAPTER ONE

INTRODUCTION

1.1 Background Information

Heavy metal contamination of water, soil and vegetables is a severe problem affecting the environment all over the world, more so in developing countries. Rapid urbanization, industrialization and increased use of agrochemicals have contributed to a great extent the accumulation of heavy metals in water, soil and vegetables (Akenga *et al.,* 2020). The high growth rate of towns, expansion of the industrial sector, increase in the number of processing and manufacturing plants have resulted in increased amount of industrial and municipal effluents (Hussain *et al*., 2019). All these effluents are drained into the sewage treatment plants and hence the resultant sewage water carries a heavy load of heavy metals and other toxicants. Urban industrial effluents and domestic wastes when improperly disposed, they are washed down by rainwater into urban rivers and streams increasing the level of contamination of water in the rivers and streams. Heavy metal contamination is also attributed to natural sources such as acid rain erosion and weathering of rocks. Anthropogenic sources such as dumping of metallic waste, waste water irrigation, mining and sewage sludge have further contributed to presence of heavy metals in the environment (Ahmed *et al.*, 2018).

The main and often the only control strategy used to reduce pollutant concentrations to ensure compliance with the water resources quality standards is individual or collective wastewater and sewage treatment before final disposal (Macedo *et al*., 2018). However, this is not the case in many cities and more so in the developing countries where heavy metals in river water are greater than World Health Organization (WHO) recommended standards for drinking water have been reported in previous studies. For example, 2.297 mg/L Cr and 1.051 mg/L Pb in Challawa River in Nigeria (Bichi & Dan'Azumi, 2010), 158 µg/L Pb and 245 µg/L Cr in Nairobi River (Njuguna *et al*., 2017). This is due to discharge of effluents to the urban river systems. Introduction of pollutants to water from both natural and anthropogenic activities not only affects the concentration of heavy metals in water but also the physicochemical properties of water such as pH, temperature, electrical conductivity (EC) and total dissolved solids (TDS). These physico chemical properties affect the colour, odor, taste and quality of water.

The use of urban stream wastewater for irrigation by marginal farmers is a common practice in urban and peri-urban ecosystems of many countries (Getachew *et al*., 2020). This is due to the scarcity of clean water in many urban cities of developing countries. Secondly, the wastewater contains significant amounts of beneficial nutrients hence farmers take advantage of the nutrients to grow a variety of crops in the urban areas (Alghobar & Suresha, 2017; Mahmood & Malik, 2014). However, irrigation with sewage contaminated river water is known to have a significant impact on accumulation of heavy metals in agricultural soils and the irrigated crops (Ahmed *et al.*, 2018; Alghobar & Suresha, 2017; Balkhair & Ashraf, 2016; Bati *et al*., 2016). This has been highlighted by previous studies which have revealed that long-term utilization of wastewater in irrigation may cause contamination of the soils and vegetables grown using such water since most heavy metals do not undergo microbial or chemical biodegradation (Khan *et al*., 2019; Ahmed *et al.*, 2018; Singh *et al*., 2009).

Consumption of crops with elevated levels of heavy metals and trace elements within a given area can lead to the emergence of epidemics (Gall *et al*., 2015; Salem *et al*., 2014; WHO, 2011). Heavy metals such as Cd, Cr, and Pb have been reported to be increasingly associated with cancer problems, kidney ailments, neurological issues and deficiency of vital body nutrients resulting in decreased body immunity (Oghenebrorie & Chudy, 2020; Cobbina *et al*., 2015).

In the treatment of industrial wastewater containing heavy metals, technologies for reduction of toxicity are often involved in order to meet technology-based treatment standards (Gunatilake, 2015). Some of the physico-chemical processes employed in heavy metal removal include; adsorption on new adsorbents, ion exchange, membrane filtration, electro-dialysis, reverse osmosis, ultra-filtration and photo-catalysis (Dula & Duke, 2019). Ultra-filtration (UF) utilizes permeable membrane to separate heavy metal macromolecules and suspended solids from inorganic solution based on the pore size (5–20 nm) and molecular weight of the separating compounds (Huang & Feng, 2019; Huang *et al*., 2015). Complexation ultra-filtration allows separating, concentrating and recovering very different metal ions from both industrial and municipal effluents (Llanos *et al*., 2010; Baharuddin *et al*., 2014).

The aim of this study was to establish the levels of heavy metal concentrations in water in two urban streams (Iini stream and Ikiwe river) flowing through Machakos town, in soil and selected vegetables (spinach and kale) irrigated by this water and additional vegetables bought from market sites in Machakos town. This study also sought to evaluate the effectiveness of modified starch polymer in removing heavy metals from water. Outcomes of this study provide important information on heavy metals, useful in subscribing to sustainable urban effluent and domestic sewage management in regard to public and environmental health.

1.2 Problem Statement

Sewage and solid waste management is a common challenge for cities in low-income countries, leading to the problem of water pollution. Kenya, generally, has large quantities of wastewater produced as sewage that is released directly into urban streams within the municipalities. Application of contaminated water to agricultural lands contaminates the soil, affects the quality of crops hence posing a health risk to humans who consume the crops grown using such water (Hamid *et al*., 2017). Machakos town has large quantities of wastewater produced as sewage from the main sewer line. However, the small sewage treatment plant available is not working to a greater extend and thus most of the sewage is released raw and directly into the urban streams causing pollution. Research on heavy metal pollution in the urban river systems in Machakos municipality is minimal and yet farmers living along these streams use this river water to irrigate their vegetables, as drinking water for their animals and some for domestic use. A large number of family farms surround the town and irrigation farming using water from the urban streams is a key economic activity within the area. Vegetable farming specifically is a lucrative business opportunity due to the growth of the population of the town, which provides a ready market for the vegetables. Consumption of vegetables irrigated using contaminated water in the river systems in Machakos municipality is exposing the consumers to possible harmful health effects. This is because the sewage-irrigated vegetables are known to accumulate substantial amounts of heavy metals in their tissues. Additionally, irrigation using contaminated water also leaves the soil contaminated. Therefore, the urgent need to determine the concentration of heavy metals in water, soil and in vegetables grown along these urban streams as well as those sold in the market. Based on the findings from this research, public awareness will be created to consumers on the safety of the vegetables and to the farmers along the river systems on the dangers of using the contaminated urban streams water to irrigate their vegetables.

1.3 Research Questions

This study sought to answer the following research questions in a bid to achieve the research objectives;

1. What are the major point sources of water pollution in Machakos municipality?
2. Which are the physical and chemical characteristics of water in Iini stream and Ikiwe River?
3. What are the levels of the heavy metals (Cd, Pb, Cr, Zn, and Cu) in the two riverine systems (Iini stream and Ikiwe River), soil, vegetables (Kales and Spinach) irrigated with water from the urban riverine systems, and those sold in the municipality?
4. What is the correlation between concentrations of heavy metal in water, soil, and vegetables grown along the two riverine systems?
5. What is the viability of application of carboxymethyl starch polymer in the removal of heavy metals from water?

1.4 Study Objectives

1.4.1 Main Objective

The main objective was to assess heavy metal (Cd, Cu, Pb, Zn and Cr) concentrations in the two urban riverine systems within Machakos municipality and in selected vegetables (spinach and kale) grown and sold in the municipality and compare them with WHO recommended levels.

1.4.2 Specific Objectives

The specific objectives that the research sought to achieve were;

1. To identify and map out the point water pollution sources in Machakos town.
2. To determine the physico-chemical characteristics (pH, temperature, TDS, EC) of water in the two riverine systems under study and compare them with WHO acceptable standards.
3. To evaluate the concentration of heavy metals (Cd, Pb, Cr, Zn, and Cu) in water from Iini stream and Ikiwe river, in soils and selected vegetables (Spinach and Kales) irrigated using water from these two urban riverine systems and those sold within Machakos town and compare them with WHO permissible levels.
4. To establish whether there is a correlation between concentrations of heavy metal in water, soil, and vegetables (spinach and kale) grown along the two riverine systems.
5. To evaluate the potential of carboxymethyl starch polymer in the removal of heavy metals from heavy metal contaminated water.

1.5 Research Hypotheses

This research was based on the following null hypotheses;

1. The heavy metal pollution in water in the two urban riverine systems (Iini and Ikiwe) within Machakos town and the soil are not influenced to a great extent by municipal effluents.
2. The physico-chemical characteristics (pH, temperature, TDS, EC) of water in the two riverine systems under study do not exceed WHO acceptable standards.
3. The concentration of heavy metals in water from the urban river systems, soil and the concentration in vegetables does not exceed the WHO set limits for irrigation water, agricultural soil and set limits for food for human consumption respectively.
4. There is no significant relationship between heavy metal concentration in the urban river water, soil and the concentration of heavy metals in selected vegetables (Spinach and Kales) grown and sold in Machakos town
5. The use of carboxymethyl starch polymer has no potential in removal of heavy metals from heavy metals from heavy metal contaminated water.

1.6 Justification of the Study

Water is a universal basic commodity with many uses for the survival of humans and animals. However, water can be rendered harmful when polluted resulting in a myriad of problems (Nzeve *et al*., 2015). Due to the creation of county governments and devolution of government services, the establishment of Machakos University, closeness of

Machakos town to Nairobi and industrial growth, the population of Machakos town is rapidly increasing. Increase in population translates to higher production of domestic waste and sewage, which has put a strain on the existing sewer system resulting in breakage or overflow of sewer lines (Figure 1.1). Additionally, the sewer treatment plant is small to adequately accommodate and treat the increasing volumes of sewage and the solid waste management system is not well coordinated. Sewage from the broken sewer lines drains into nearby urban streams contaminating the water. Furthermore, during the rainy season, the sewer lines are likely to overflow and drain into the riverine system within the municipality.

Figure 1.1: Raw sewage leaking directly into Iini Stream, in Machakos town (Location -1.5225467 and 37.2713401)

The rapid population growth has also created an increased demand for vegetables and food crops causing farmers living along the urban streams to use this sewage contaminated stream water to irrigate vegetables (Figure 1.2). The vegetables are later harvested, sold to traders in Machakos town and consumed without proper validation of their quality for consumption. The urban streams in Machakos municipality face major pollution from domestic, agricultural, sewer effluents and other anthropogenic sources.

Generally, the status of the Machakos town-sewage treatment plant is questionable. These scenarios were indicators that water from the urban streams in Machakos town had viable heavy metal contamination, and thus subject to investigation on the level of the contaminants. The research intended to verify the quality of water within the urban streams and ascertain whether it met the recommended standards for various uses under which it is subjected so as to ensure the safety of residents and the environment.

Figure 1.2: Vegetables grown using the sewage contaminated urban stream water and the state of the urban stream water in Machakos municipality

It was of essence that farmers on the banks of the rivers and the public in general, be informed of the quality of the water regarding agricultural use and the relevant county government agencies be informed for remedial measures where the quality is below recommended standards. Consumers in Machakos town will be made aware of the quality of vegetables that are grown and sold within Machakos municipality.

CHAPTER TWO

LITERATURE REVIEW

2.1 Sources of Water Pollution

Water pollution is contamination of water by an excess of a substance that can cause impairment of the ecosystem and the people (Singh & Yadav, 2020). Water pollution poses a serious problem to the environment and to the lives of humans, animals, and plants. There are numerous laws concerned with water pollution. However, the issue of water pollution continues to be a worldwide problem, especially in urban areas (Macedo *et al*., 2018). Water sources are increasingly becoming polluted by direct and indirect pollution sources. Direct pollution sources include effluent from factories, refineries, waste water treatment plants, septic tanks, runoff from the farms and constant leakage of sewer systems among others (Gupta *et al*., 2017; GOK 2009). Indirect sources of water pollution include contaminants that enter the water supply system from soils/groundwater systems and atmosphere via rainwater (Singh & Yadav, 2020).

Sewage and solid wastes have been termed as major sources of water pollution because they introduce high volumes of organic and non-biodegradable wastes (Gupta *et al*., 2017). Industries have been termed as another source of water pollution as their wastes that contain dyes, acids, alkalis and other chemicals are emitted into water bodies as effluents. Agro-chemical inputs such as fertilizers, pesticides and herbicides which are widely applied in crop fields to enhance productivity also contribute significant pollutants to water bodies (Singh & Yadav, 2020; Nzeve, 2015). According to Aywa (2017), river water is open to many polluting agents especially those that gain entry from urban centers and that both bacterial and chemical pollution poses a risk to the health status of people.

2.2 Physical and Chemical Characteristics of Wastewater

Wastewater is used water from any combination of domestic, industrial, commercial or agricultural activities, surface runoff, and any sewer flow. Wastewater contains physical, chemical and biological pollutants that contribute to the various characteristics of water.

2.2.1 Temperature

Temperature is important to aquatic plants and animals and to the overall health of a water body. Changes in water temperature affect water quality and aquatic biota (Choudhary *et al*., 2006). Thermal pollution mainly emanates from human related activities. Most industries are located near riverbanks due to the large amounts of water required during industrial processes. These industries release large amounts of heat into the water bodies altering the physical, chemical and biological composition of aquatic ecosystems. Increased water temperature may also emanate from exposure to natural radiant heat from the sun. High water temperature lowers the oxygen content of water, alters the reproductive cycle of organisms causes and other physiological changes, causing difficulties for aquatic life (Gupta *et al*., 2017).

2.2.2 pH

Water pollution such as acid rain alters plants surrounding and high pH level can harm or kill the plants. Atmospheric sulfur dioxide and nitrogen dioxide emitted from natural and human-made sources like volcanic activity and burning of fossil fuels, interact with atmospheric chemicals, including hydrogen and oxygen, to form sulfuric and nitric acids in the air (Xiao *et al*., 2019). These acids fall down to earth through precipitation in the form of rain or snow. Once acid rain reaches the ground, it flows into waterways that carry its acidic compounds into water bodies. Acid rain that collects in aquatic environments lowers water pH levels and affects the aquatic biota. Dissolved chemical compounds in domestic or commercial effluents also have an impact on the pH of water once the effluent gets to water bodies. pH levels that are very high or low can be harmful to living organisms in water.

2.2.3 Total Dissolved Solids

Water is termed as a universal solvent because of its ability to dissolve many compounds. As water travels through the atmosphere and the river systems it dissolves many minerals and washes them away. A certain amount of dissolved salts is necessary for aquatic life as it helps in flow of water in and out of an organism’s cell. However, changes in amount of salts in water can be harmful to the aquatic life (Mohammad *et al*., 2016). Changes in amount of salts in water bodies can occur naturally due to variations in evaporation and freshwater flow rate or due to human influence emanating from discharge of effluent into the water bodies.

2.2.4 Electrical Conductivity (EC)

EC is a measure of the ionic activity of water in terms of its capacity to transmit electric current. It depends on the presence of ions, on their total concentration, mobility and temperature of measurement (Golnabi *et al*.,2009). Higher value of conductivity shows higher concentration of dissolved ions. Pure water is poor conductor of electricity. Electrical current flow in water is by ions in water and thus the electrical conductivity increases with increase in the concentration of water dissolved ionic species.

2.3 Use of Sewage Effluent for Irrigation

Wastewater can be a resource depending on the degree of treatment and dilution since it is rich in nutrients, inorganic and organic compounds. The application of sewage water to agricultural land is presently emphasized as a means to relieve the general waste accumulation and also a widespread practice in areas that experience water deficiencies (Chaoua *et al*., 2018). Experience gained in Israel over a period of more than 25years has shown that good yields can be obtained by irrigation of agricultural land with secondary treated wastewater (Tal, 2016). In recent years, it has become an important agronomic procedure because wastewater contains some amount of nitrogen, phosphorus and potassium nutrients and can contribute to organic matter recycling and restoring the soils fertility (Alghobar & Suresha, 2017). The value of nitrogen, phosphorus and other nutrients are not objectionable due to the importance of such minerals in plant growth. However, heavy metals and other pollutants contained in sewage water are a great disadvantage considering their toxicity even at low concentrations. The heavy metals in wastewater tend to accumulate in the top layers of soil in various degrees of availability. With prolonged use of sewage effluents for irrigation, heavy metals are liable to build up to toxic levels and are introduced into the food chains by way of animal feed and human food. Additionally, the quality of irrigation water has a considerable impact on the type of plants that can be grown, the productivity of the plants, the quality of the plants and the physical conditions of the soil (Alghobar & Suresha, 2017; Singh *et al*., 2009). There are various reports (Akenga *et al*., 2020; Maina *et al*., 2019; Wambua *et al*., 2018; Sayo *et al*., 2020; Singh, 2013) where sewage water is being used for the irrigation of edible plants and it is a matter of great concern due to the presence of pollutants particularly, toxic metals.

2.4 Heavy Metals

Heavy metals refer to metallic chemical elements that have relatively high density and are toxic or poisonous at low concentrations (Tchounwou *et al*., 2012). Examples of heavy metals include Mercury (Hg), Cadmium (Cd), Arsenic (Ar), Chromium (Cr), Lead (Pb) and Thallium (Th). As trace elements some elements such as Zinc (Zn), Copper (Cu) and Selenium, are vital in maintaining the metabolic processes of the human body. Heavy metals can emanate from both natural and anthropogenic sources and end up in different compartments of the environment i.e. air, water, soil and plants (Masindi & Muedi, 2018). Heavy metals are of great concern because of their persistence in the environment, bioaccumulation along food chains and their toxicity even in low concentrations.

2.4.1 Sources of Heavy Metals

Cadmium is released from zinc refining as a key by-product since as the metal is found to occur naturally within the raw ore of zinc (Council, 2003). Cadmium is primarily used in the manufacture of rechargeable nickel/cadmium batteries. Cadmium is also used as a coating in aerospace and marine applications as it provides a good corrosion resistance to the environmental stresses (Monitoring & Fate, 2014). Other uses of cadmium are; as pigments, stabilizers for PVCs, in alloys and in electronics (Genchi *et al*., 2020). Cadmium is also present as an impurity in by-products, in phosphate fertilizers, detergents and refined petroleum products. Volcanic activity, gradual erosion, abrasion of rocks and soils and forest fires are also among the reasons for increase in Cd concentrations in the atmosphere.

Copper is a common naturally occurring substance in the human habitat and spreads throughout the surroundings through natural pathways. Copper in the environment can also originate from anthropogenic sources such as waste dumps, domestic wastewater, combustion of fossil fuels and wastes, wood production and phosphate fertilizer production. Copper emanates from copper compounds that are commonly used in agriculture to treat plant diseases like mildew, in water treatment and as a preservative for wood, leather and fabrics (Georgopoulos *et al*., 2011). Copper pipes, as well as additives designed to control algae growth are said to be an additional common sources of copper in drinking water (Oskarsson & Norrgren, 2011).

Lead is ubiquitous in the environment because of its widespread human use. Environmental background levels vary depending on historic and ongoing uses in the area. Lead is among the most recycled non-ferrous metals and its secondary production has therefore grown steadily in spite of declining lead prices. Its physical and chemical properties are applied in the manufacturing, construction and chemical industries. It is easily shaped and is malleable and ductile. There are eight broad categories of use; batteries, petrol additives, rolled and extruded products, alloys, pigments and compounds, cable sheathing, shot and ammunition (Zhang *et al*., 2015). Coal like many other minerals, rocks and sediments, usually contains low concentrations of lead. A number of other industrial activities such as iron and steel production, copper smelting and coal combustion are regarded as additional sources of lead emissions into the atmosphere. The presence of lead water pipes in old houses can be another important source of lead particularly in areas with soft water. In certain areas, lead-containing paint in old houses can be an additional source as are other diverse uses such as lead solders, ceramic glazes, cosmetics and folk medicines (Seema *et al*., 2013).

Zinc is an element commonly found in the Earth's crust. It is released to the environment (air, water, soil) from both natural and anthropogenic sources. However, releases from anthropogenic sources are greater than from natural sources. Erosion of minerals from rocks and soil is a natural pathway of introduction of zinc into water. The anthropogenic sources of zinc in the environment include; as by-products of steel production, coal fired power stations, burning of waste materials, electroplating, metallurgic operations involving zinc and use of commercial products containing zinc such as wood preservatives that contain zinc (Nzeve, 2015; Rico *et al*., 2005). Zinc in water is also through leaching from fertilizers, effluents of commercial industries during mining and smelting (metal processing) activities. Urban runoff and municipal sewages have also been referred as additional sources of Zn into aquatic ecosystems (Nzeve, 2015).

Chromium enters the environment through both natural processes and human activities. Chromium is found in paint pigments, cement, metal alloys, paper and other materials (Kinuthia *et al*., 2020). Cr is also found in industrial wastes such as tannery wastes, leather manufacturing wastes and municipal sewage sludge. Chromium can exist as chromium III or chromium VI. Increases in Chromium III are due to leather, textile, and steel manufacturing while chromium VI enters the environment through some of the same channels such as leather and textile manufacturing and due to industrial applications such as electro-painting and chemical manufacturing. Groundwater contamination may occur due to seepage from chromate mines or improper disposal of mining tools and supplies, and improper disposal of industrial manufacturing equipment.

2.4.2 Environmental Impact of Heavy Metals

2.4.2.1 Heavy Metals in Water

Some heavy metals have higher solubility in water compared to other heavy metals. Therefore, the rate of propagation of such in nature is higher and yet some are not essential elements for plant and human life. When heavy metals and their compounds are released into water, they dissolve and are carried in surface waters either in the form of compounds or as free metal or, more likely bound to particles suspended in the water. Even though metals bind strongly to suspended particles and sediments, there is evidence to suggest that some water-soluble metal compounds do enter groundwater (Begum *et al*., 2009). A metal that enters water eventually collects in the sediments of rivers, lakes, and estuaries. Metals in surface water can be propagated to far distances as free ions or suspended on sludge particles. Due to their water-soluble properties, heavy metals are taken into biological systems by a plants and marine organisms. The metals exhibit long-term persistence in the environment and thus easily accumulate in aquatic plants and aquatic organisms over time.

Heavy metals may enter the natural waters by weathering of metal containing rocks, direct discharge from industrial operations, leaching of soils, among others. In the aquatic environment, heavy metals can undergo reduction, oxidation, sorption, desorption, dissolution, and precipitation (Oliveira, 2012). The aqueous solubility of the metals is a function of the pH of the water. Under neutral to basic pH, metals will precipitate and conversely under acidic pH they will tend to solubilize (Oliveira, 2012).

2.4.2.2 Heavy Metals in Soil

When heavy metals end up in soil, they strongly attach to organic matter and minerals. As a result, they remain in the soil after release and scarcely enter groundwater. Heavy metals can interrupt the activity in soils, as they negatively influence the activity of microorganisms and earthworms resulting in the slowdown of decomposition of organic matter. Heavy metals can seriously influence the proceedings of farmlands, depending on the acidity of the soil and the availability of organic matter (Kumar *et al*., 2007). When released into soil, they become strongly attached to the organic material and other components (e.g., clay, sand, etc.) in the top layers of soil and may not move very far and end up accumulating in the soils after deposition.

Heavy metal accumulation in soils used for agricultural purposes may lead to contamination of the environment at the same time have an effect on the quality and security of food crops grown on such soils (Bigalke *et al*., 2017; Sharma *et al*., 2016). Soils in farms under irrigation have been reported to accumulate heavy metals including Zn, Ni, Cd, Pb, and Cr within the soil, hence, growing crops in farms containing elements such as Cr, Cd and Ni have a greater chance of becoming a health hazard for consumers (Alghobar & Suresha, 2017). Accumulation of metals in soil may as well be caused by extended usage of polluted irrigation waters

The concentration of heavy metals in soils may vary considerably according to the natural composition of rocks and sediments that compose them. The levels of heavy metal in the soil may increase mainly through anthropogenic deposition, such as atmospheric deposition, also dumping of heavy metal-bearing liquids and solid wastes. As in aquatic environment, once in the soil or sediment, heavy metals undergo a variety of transformations, such as oxidation, reduction, sorption, precipitation, and dissolution. For example, the oxidants present in the soil can oxidize Cr(III) to Cr(VI) (Oliveira, 2012).

2.4.2.3 Heavy Metals in Vegetables

Vegetables are a key source of minerals, vitamins, and fiber important for human health and nutrition (Bett *et al*., 2019; Wong *et al*., 2019). Exotic vegetables such as kale, spinach and cabbage account for 90% of the vegetables consumed in Kenya compared to 3.7% of indigenous vegetables consumed at any given time (Otieno, 2013). The ever increasing population provides a ready market for leafy vegetables thus increasing the popularity of leafy vegetable farming in the urban areas of developing countries (Kacholi, 2018; Balkhair & Ashraf, 2016; Kombe, 2005). However, consumption of vegetables grown in the urban areas has increasingly become a matter of interest to both consumers and public health authorities due to likely contamination caused by use of polluted urban streams water for irrigation of vegetables. Previous studies have reported that urban waste water effluent contains a high concentration of heavy metals, which are easily absorbed by vegetables thus posing a health risk to consumers (Hussain *et al*., 2019; Shaheen *et al*., 2016). Industrial effluents, municipal sewage, solid waste disposal, excessive application of pesticides, inappropriate use of fertilizers and vehicular traffic emissions are attributed to the increased concentration of heavy metals in the vegetables (Bi *et al.,* 2018). A numerous studies affirm the positive correlation of heavy metals in vegetable tissues and heavy metals in surrounding habitat. Crops grown in polluted soil or irrigated with polluted water may thus contain increased heavy metal concentrations.

At trace levels, some of the heavy metals such as copper and zinc are essential elements that play important roles in plant metabolism. However, they can be toxic at high concentrations (Sayo *et al*., 2020). The other heavy metals, such as Cd, Hg, and Pb have no known essential role in plants and are toxic at even trace concentrations. The major pathways of elements in vegetable crops are their developing media that includes air, soil and water and the elements are absorbed through their foliage or roots. Vegetables absorb sufficient amount of water for their different requirements. Metals present in this available water arrive in vegetable tissue with the water and accumulate in various parts of plant bodies, these metal contents may affect the plants activities and generate some physical changes in plants. Results of various studies show that heavy metals mainly accumulate in roots, followed by stems and leaves of a plant (Akenga *et al*., 2020; Singh, 2013).

The process of uptake and accumulation of heavy metals by different plants depends on the concentration of available metals in soils, solubility sequences and the plant species growing on these soils (Singh, 2013). Uptake of micro-nutrients and heavy metals by vegetables and their accumulation in different plant parts have been assessed and wide variation in the mode of accumulation has been observed for different micro-nutrient and heavy metals. The uptake and accumulation of heavy metals in the edible part of green tissue represents a direct path way of incorporation of heavy metals into the human food chain.

2.4.3 Human Exposure to Heavy Metals

The major exposure to cadmium is via food, atmospheric deposition, fertilizer application and uptake by food crops. Additional exposure to humans is through cadmium in ambient air and drinking water. Cigarette smoke is also a major route of exposure of Cd to humans through inhalation (Monitoring & Fate, 2014).

Copper is found in different kinds of food, in drinking water and in air at varied concentrations. Thus, eating, drinking and inhalation are key routes of human exposure to eminent quantities of copper. Exposure to copper through inhalation is to a small extent as copper concentrations in air are usually quite low. In houses that still have copper plumbing, copper is released directly into drinking water though corrosion of the pipes and thus people living in such houses are exposed to higher levels of copper than most people (Oskarsson & Norrgren, 2011). Skin contact with soil, water and other copper-containing substances in the working environment is also another route of human exposure to copper. Copper absorption in the human body is necessary since copper is a trace element that is essential for human health. However, too high concentrations of copper can still cause eminent health problems.

Lead is much present in the environment emanating from both anthropogenic and natural sources. Human exposure to lead can be through several ways; food, drinking water, dust from lead containing paints, and soil. For young children, water, food and air are the major routes of lead exposure. On the other hand, water, air and milk formula are the significant sources of exposure to infants up to 5months. Although most people receive the bulk of their lead intake from food, in specific populations other sources may be more important, such as water in areas with lead piping and plumbo solvent water, air near point of source emissions, soil, dust, paint flakes in old houses or contaminated land (Zhang *et al*., 2015).

Zinc can enter the body through the digestive tract when we eat food or drink water containing it. Humans are also exposed to zinc compounds present in the food we eat. Food may contain levels of zinc ranging from approximately 2 ppm (e.g., leafy vegetables) to 29 ppm (meats, fish and poultry). Zinc is also present in most drinking water. Drinking water or other beverages may contain high levels of zinc if they are stored in metal containers or flow through pipes that have been coated with zinc to resist rust. Zinc can also enter through your lungs if you inhale zinc dust or fumes from zinc-smelting or zinc-welding operations in your working area. The amount of zinc that passes directly through dermal contact with the skin is relatively small. The zinc is stored throughout the body. Zinc increases in blood and bone most rapidly after exposure. Zinc may stay in the bone for many days after exposure. Zinc is an essential element needed by the body in small amounts. If taken more than the recommended daily amount of supplements containing zinc, you may have higher levels of zinc exposure (Jayant *et al.*, 2013).

Inhalational exposure to Cr (VI) affects only a small portion of the population, mainly by occupational exposures. Oral exposure to Cr (VI) is widespread and affects many people throughout the globe. The primary source of oral exposure to Cr for non-occupational human populations comes from food and drinking water. Cr levels in the food range from <10 to 1300 μg/kg, with the highest amount in meat, fish, fruits, and vegetables (Sun *et al.*, 2015). The concentration of Cr in uncontaminated water is very low, about 1–10 μg/L in rivers and lakes and 0.2–1 μg/L in rainwater, with an average concentration of 0.3 μg/L in ocean water (Shanker, 2011). Dermal exposure to chromium may occur during the use of consumer products that contain chromium, such as wood treated with copper dichromate or leather tanned with chromic sulfate.

2.4.4 Effects of Heavy Metal Contamination on Human Health

Absorption of Cd mainly occurs through the respiratory tract and to a smaller extent through the gastrointestinal tract. When Cd enters the body, it is transported to different body parts through the blood stream. Cadmium excretion from the body is slow and thus it ends up accumulating in the body parts. Chronic toxicity of Cd has been associated to damages of respiratory, renal, skeletal and cardiovascular systems as well as development of cancers of the lungs, kidney, prostrate and stomach (Kinuthia *et al*., 2020).

Copper is an essential substance to human life, but in high doses it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Exposure to high levels of copper can cause stomachaches, diarrhea, vomiting, dizziness and irritation of the eyes, nose and mouth. Extremely high intakes of copper can result liver and kidney damage (Anant *et al*.,2018). Decline in intelligence in young adolescents as result long-term exposure to high concentration of copper has been reported in scientific articles (Georgopoulos *et al*., 2011). Industrial exposure to copper via dusts, fumes and mists can cause metal fume fever, which greatly affects nasal mucous membrane. Chronic copper poisoning results in hepatic cirrhosis, renal disease, Wilson 's disease, demyelization, brain damage, and copper deposition in the cornea (Araya *et al*., 2007). People with Wilson's disease are at greater risk for health effects from overexposure to copper. Infants and children under 1-year-old are unusually susceptible to the toxicity of copper. Infants and children under 1 year old are in a high-risk category because they have not yet developed the homeostatic mechanisms for clearing copper and preventing its entry via the intestine (Georgopoulos *et al*., 2011).

Human exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure. Lead poisoning is so severe as to cause evident illness. At certain concentrations, there is clear evidence that lead can have indirect effects, particularly on neuropsychological developments in children. Different effects occur over a wide range of lead levels, with the developing fetus and infant being more sensitive than the adults. High levels of exposure may result in toxic biochemical effects in humans, which in turn cause problems in the synthesis of hemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system (Wani *et al*., 2015). The high levels have also been associated with cardiovascular and carcinogenic effects in humans (Papanikolaou *et al*., 2005).

Zinc is the second most abundant essential trace metal in the body after iron and is essential for growth and survival. The role of zinc in the human body has been extensively been discussed by Gammoh and Rink, 2019. The great industrial importance of Zn has made this element a potential hazard to vegetable consuming humans. Despite the apparent biological importance of zinc, acute as well as chronic exposure to overly high concentration of zinc could also bring detrimental impact to human health. The manifestation of acute zinc poisoning could include nausea, stomach cramps, vomiting, diarrhea, fever and lethargy (Wei *et al*., 2019; Saskatchewan, 2007). While long-term chronic exposure to excessive zinc levels could result in metabolic interference with other trace elements. Chronic enriched zinc intakes could result in various chronic effects in gastrointestinal, hematological, and respiratory system along with alteration in cardiovascular and neurological systems of people (Nriagu *et al*., 2011). Ingesting high levels of zinc for several months may also cause anemia, damage the pancreas, and decrease levels of high-density lipoprotein (HDL) cholesterol. Human beings supplemented with 300 mg zinc per day have been characterized to have elevated low – density lipoprotrein (LDL) cholesterol and reduced high-density lipoprotein (HDL) cholesterol (Nriagu *et al*., 2011). The levels of zinc that produce adverse health effects are much higher than the Recommended Dietary Allowances (RDAs) for zinc of 11 mg/day for men and 8 mg/day for women. If large doses of zinc (10-15 times higher than the RDA) are taken by mouth even for a short time, stomach cramps, nausea, and vomiting may occur (Laura *et al*.,2010).

Chromium on low-level exposure can irritate the skin and cause ulceration. Long-term exposure of Cr can cause kidney and liver damage, and damage to circulatory and nerve tissue. Chromium often accumulates in vegetables, adding to the danger of eating vegetables that may have been exposed to high levels of chromium. Chromium III is essential for regular operation of human vascular and metabolic systems as well as combating diabetes, however, too much chromium III may result in severe skin rash, or other more serious symptoms. Chromium VI is the most dangerous form of chromium and may cause health problems including: allergic reactions, skin rash, nose irritations and nosebleed, ulcers, weakened immune system, genetic material alteration, kidney and liver damage, and may even go as far as death of the individual (Chatterjee, 2015).

2.5 Transfer Factor (TF)

Transfer factor is a key component in assessing bioaccumulation of heavy metals through the food chain. Vegetables obtain nutrients including metals from the soil for growth. Vegetables absorb heavy metals from the soil and water through ionic exchange, redox reactions, dissolution or precipitation (Adamo *et al*., 2014; Chowdhury & Rasid, 2016). When the concentration is high enough, trace metals can accumulate in the roots, stems and leaves of vegetables. Higher TF values (≥1) indicate higher metal absorption from the soil by vegetables that can cause harm to human health. On the contrary, a TF value below 1 indicates a poor vegetable response to metal absorption and vegetable is safe for human consumption (Prabasiwi *et al*., 2020). However, if TF value is higher than 1, it cannot be concluded that soil is the only source of heavy metal contamination in vegetables. Contaminated vegetables consumed by human, are a threat to the human health.

2.6 Complexation Ultra-filtration

In the treatment of industrial wastewater containing heavy metals, technologies for reduction of toxicity are often involved in order to meet technology-based treatment standards (Gunatilake, 2015). Researchers have tried physical, chemical and biological methods. Some of the physico-chemical processes employed in heavy metal removal include; adsorption on new adsorbents, ion exchange, membrane filtration, electro-dialysis, reverse osmosis, ultra-filtration and photo-catalysis (Gunatilake, 2015). Ultra-filtration (UF) utilizes permeable membrane to separate heavy metals, macromolecules and suspended solids from inorganic solution on the basis of the pore size (5–20 nm) and molecular weight of the separating compounds.

Polymer supported ultra-filtration (PSU) also called complexation ultra-filtration allows separating, concentrating and recovering very different metal ions from both industrial and natural effluents. The selectivity of this process depends mainly on both the affinity of the selected polymer to the target metals and the selected working conditions (Llanos *et al*., 2010). Polymer-supported ultra-filtration (PSU) technique adds water soluble polymeric ligands to bind metal ions and form macromolecular complexes which can be ultrafiltered producing a free targeted metal ions effluent (Llanos *et al*., 2010). Recently polymer supported ultra-filtration has shown to be a promising technique in the removal of heavy metals in solution. Past studies have investigated the removal of toxic heavy metals such as Cu, Ni and Cr from wastewater solutions. Polyethylenimine (PEI) has been reported to complex efficiently Cd, Cu, Cr, Pb and Zn and reduce their permeate levels to less than 4ppm (Masotti *et al*., 2009).

Starch is one of the most important biomass and has the hydroxyl functional groups that can be easily modified by chemical reactions. The versatile modifications on starch allow the introduction of other functional groups such as, esters, carbonyl, carboxylate, xanthate, phosphate/phosphoryl, carbamate, and acrylate, with affinity for some inorganic and organic water contaminants, *via* molecular, electrostatic and coordinative interactions resulting in the removal of contaminants from water (Akinterinwa, 2020). Cross-linking reaction is the introduction of inter-and intra-molecular bonds which results in a three-dimensional network in the starch polymer matrix. It affects morphological reinforcement and mechanical stability of the starch polymer matrix, hence the granules. The three-dimensional network in cross-linked starch has also create pores which may serves as trapping sites for contaminants in a phenomenon referred to as ultra-filtration. Most of the starch derivatives can be degraded in the natural environment and an important modification of the starch hydroxyl is carboxymethylation (Wang *et al*., 2010). Carboxymethyl starch (CMS) is a cold water-soluble starch derivative having wide applications in the fields of pharmaceutical, textile, paper making, adhesive and absorbent (Li *et al*., 2011; Spychaj *et al*., 2013). Carboxymethylation process introduces a hydrophilic carboxymethyl group ($-CH_2COO^-$) to starch derivatives (Musarurwa & Tavengwa, 2020). Carboxymethyl group is constituted by carbonyl (C=O) and carboxylate ($-COO^-$) functional groups, and these have been associated with heavy metal adsorption *via* coordination, molecular bonding and ion-exchange processes (Akinterinwa, 2020). The carboxymethylated functional groups can chelate many heavy metal ions, so this kind of modification could give starch an ability of removal and recovery of the heavy metal ions.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The study area lies within the area bounded by the longitudes 37.28036 E37º16’49.2829’’and 37.35522 E37º21’18.78778’’ and latitudes -1.53076 S1º31’507361’’ and -1.522425 S1º31’27.29809’’ (Figure 3.1). The research was carried out in two urban streams in Machakos municipality, Kenya. There are a high number of family farms surrounding the two streams and irrigation farming is actively taking place in the farms. Farming of vegetables is a key economic activity within the municipality due to growth of human population that provides a ready market for the vegetables. In the area of study, there are small scale industries involved in production of consumer goods such as plastics, furniture textile and food processing. The key areas of interest in this study are Iini stream and Ikiwe River where farming of vegetables takes place.

3.2 Research Design

This study was a case study that used experimental research design. The study made use of an experimental approach to carry out the laboratory analysis to collect relevant data. The laboratory analysis was done in accordance with scientific guidelines. The research objectives, questions, samples, sampling sites, and analytical procedures were predetermined and numbers and statistics used to analyze and explain its findings.

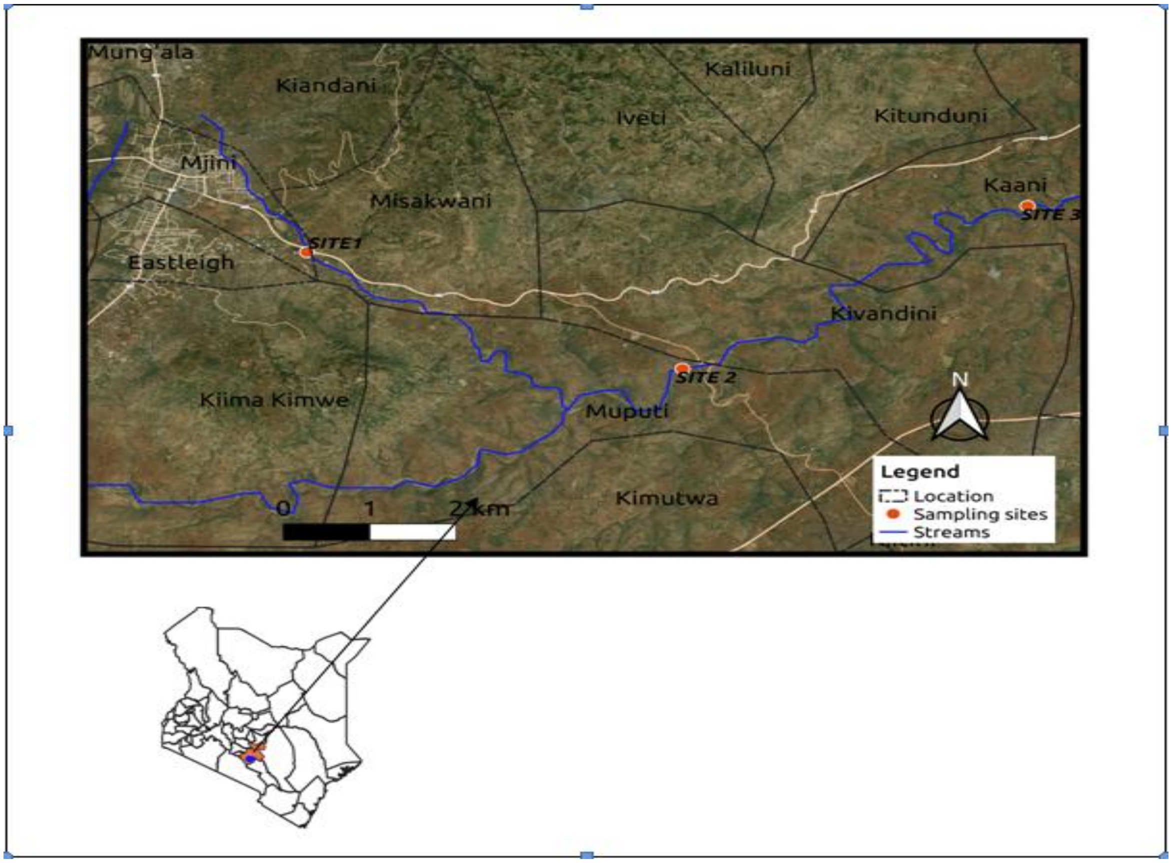

Figure 3.1: Map of the study area

3.3 Selection of Sampling Sites

Three water-sampling sites (site 1, site 2 & site 3) which lie between discharge point and irrigation point were randomly selected. Sampling site selection was based on economic activity, suspected point source pollution and land use patterns. The first site (Mwanyani) is on latitude S1^{o}31$^{'}$50.7361 and longitude E37^{o}16’49.2829, just after Machakos town where there is much direct entry of sewage into the urban stream. The second site (Ikiwe - upstream) is on the upper side of Ikiwe river latitude S1^{o}33$^{'}$4.16645 and longitude E37^{o}19$^{'}$20.43839$^{''}$ to which Iini stream drains its waters. The third site is on the lower side of Ikiwe River (Ikiwe - downstream) on latitude S13º1’27.40928 and longitude E37º21’18.88555 where there is much dilution of the water. Water, soil and vegetables grown along these three sites were collected in triplicates once every month for a period of five months. Additional vegetable samples (kale and spinach) were collected from Machakos' main open-air markets and from supermarkets in Machakos town. Vegetables from the farms are usually sold in these markets. The sampling was done during the dry season for a period of five months (June to October).

3.4 Mapping of Point Source Water Pollution

A transect walk was carried out round Machakos town and its environs to identify point pollution sources in residential, commercial and industrial areas within Machakos town. Geographical Position System was used to obtain geographical coordinates of point sources of pollution during the transect walk. The coordinates were then used to develop a map using Geographical Information System – Arc GIS.

3.5 Sampling

3.5.1 Physicochemical Parameters

Physicochemical parameters of water; temperature, pH, total dissolved solid (TDS) and electrical conductivity (EC) were measured on site using standard meters (Hanna HI 99121-pH meter and HI 99300 EC/TDS meter).

3.5.2 Sampling of Water

Polyethylene water sample bottles were pre-cleaned by rinsing them with metal-free soap, soaked in 10% HNO_3 overnight and finally washed with de-ionized water. 500 mL water samples from the three sampling sites were collected in the pre-cleaned high-density polyethylene bottles in triplicates. Prior to taking the actual samples, the sampling bottles were rinsed twice with the sample water at each site then acidified with 2 mL of nitric acid (analytical grade) to avoid precipitation, adsorption to container wall and microbial degradation. The water samples were immediately transported in iced cool box to Kenya Plant Health Inspectorate Service (KEPHIS) Analytical and Chemistry laboratory, Nairobi for heavy metal analysis.

3.5.3 Sampling of Vegetables

Selected vegetables grown in the study area, that is *Spinaciaoleracea* (spinach) and kales grown using water from the riverine systems were bought from farmers farming along the three sites of the sampling zone. Additional spinach and kale vegetable samples were bought from the main open market in Machakos town where the farmers sell their produce and from the main supermarkets in Machakos town. In each sampling site, 1 kg of each type of vegetable was collected and put in separate well-labeled bags indicating the site and date of sampling. Thereafter, the samples were transported to KEPHIS Chemistry and Analytical laboratory, Nairobi for determination of heavy metals.

3.5.4 Sampling of Soil

Soil from the same vegetable farms irrigated with water from the river systems was collected by scooping a monolith 10x10x15cm size using a plastic scooper from the three sampling sites. The soil samples from each sampling site were collected in triplicates. Rocks and leaves were removed from the soil and the soil samples stored in well-labeled pre-cleaned polyethylene containers. The soil samples were then transported to KEPHIS laboratories in Nairobi for heavy metal analysis

3.6 Preparation of Samples and Heavy Metal Analysis

3.6.1 Water Samples; Digestion and Heavy Metal Analysis

Water samples were filtered through a 0.45 µm cellulose acetate membrane filter before heavy metal analysis. The filtered water was digested in a tri acid mixture (HNO_3, HCl and $HClO_4$, ratio 5: 1: 1) at 150 ºC for at least 20 minutes (Nazir *et al*., 2015). The mixture was held at this temperature for another 20 minutes then allowed to cool. After cooling, 50 mL of the digested sample was quantitatively transferred into a 250 mL volumetric flask and filled to the mark using de-ionized water then stored at 4 ºC in a refrigerator ready for heavy metal analysis. Heavy metals analysis (Cd, Pd, Cr, Zn and Cu) in the water digests and blanks was determined using inductively coupled plasma mass spectrometer (ICP-MS).

3.6.2 Vegetable Samples; Drying, Digestion and Heavy Metal Analysis

The vegetables were oven-dried at 100 ºC then ground into powdered form. 1.5 g of vegetable powder sample was added to 15 mL tri acid mixture (HNO_3, $HClO_4$, HCl) at 150 ºC and held at this temperature in a microwave oven until the transparent solution appeared (Ali & Al-Qahtani, 2012). The digests were passed through a pre-washed filter and 50 mL of the filtrate made up to 250 mL using de-ionized water in a volumetric flask. The filtrate of vegetables was then analyzed using inductively coupled plasma mass spectrometer (ICP-MS) for Cd, Pb, Cr, Zn, and Cu heavy metal concentrations

3.6.3 Soil samples; Drying, Digestion and Heavy Metal Analysis

The soil samples were dried in an oven, sieved through a 2 mm sieve and stored in a labeled polythene sampling bag. 1g of the dried soil sample was digested using 15 mL tri acid mixture i.e. HNO_3, $HClO_4$, HCl at 150 ºC until a transparent solution appeared (Bi *et al*., 2018). 50 mL of the soil digest was placed in a volumetric flask and made up to 250 mL using distilled water. The solution was run through an ICP-MS for determination of Cd, Pb, Cr, Zn, and Cu heavy metal concentrations.

3.7 Complexation Ultra-filtration

3.7.1 Carboxymethylation of Starch

Carboxymethyl starch was prepared by etherification of starch using sodium monochloroacetate in alkaline conditions (Musarurwa & Tavengwa, 2020; Spychaj *et al*., 2013). 6.1644g of dry potato starch was weighed into 250 mL heating flask and 10 mL ethanol-water mixture containing 10 mmol sodium hydroxide was added to it and stirred thoroughly. The starch alkalization process was carried out at 35 ºC for 45 minutes. This was then followed by addition of 2.795 g sodium monochloroacetate. The etherification was carried out for 100 minutes at 45 ºC. The product was washed with 85% ethanol and filtered to remove other salts formed during the reaction. Washing and filtering was repeated three times. The product was then dried in an oven at 313 K for 24 hours.

3.7.2 Characterization of Synthesized Carboxymethyl Starch (CMS)

The synthesized CMS Fourier Transformation Infrared spectra of the samples were measured by KBr pellet method on Nicolet Nexus FT-IR spectrometer in 4000-400cm^{-1} wave number range.

3.7.3 Removal of Cd, Cu, Pb, Zn and Cr

Working solutions were prepared by dissolving standard Cd, Cu, Pb, Zn and Cr heavy metal ion stock solutions. 1.54g of CMS was added to each sample and the mixture magnetically stirred for 40 minutes to ensure complete chelating of carboxymethyl starch and heavy metal ions. The mixture pH of 7 was maintained by adding 0.1M NaOH. The resulting mixtures were then ultra-filtered. The working solutions and the filtrates were later digested and analyzed for concentration of heavy metals using ICP-MS. Percentage chelating effect was determined using the equation;

$$\%\,\boldsymbol{Chelation} = \frac{\boldsymbol{Ci - Cf}}{\boldsymbol{Ci}} \times \mathbf{100}$$

where Ci is the concentration before addition of CMS and Cf is the concentration after addition of CMS and ultra-filtration.

3.8 Calibration and Quality Control Analysis

Standard series of 0, 10, 20, 30, 50 and100 ppb of the ICP – MS were used to prepare a calibration that had a minimum of five points inclusive of the blank. The standards were prepared for each metal from their stock solution to calibrate the instrument. The detection limit of ICP-MS was 0.5 ppb. Analytical Grade chemicals were used in sample preparation. Double de-ionized water was used for solution preparation and glassware washed with 10% HNO_3. Precision and accuracy of analysis was checked through repeated analysis against European standard reference material (CEC278K) for vegetables, water and soil for heavy metals.

3.9 Statistical Data Analysis

The data was analyzed using Minitab Statistical Software, version 19. The significant difference ($p \leq 0.05$) of heavy metal concentrations in vegetables, soil, and water among the different sampling sites was tested using One-way Analysis of variance (ANOVA). Where there were significant differences in heavy metal means, post- hoc Tukey test was used to separate the means. Pearson correlation analysis was done to determine the correlation between heavy metals in soil, water and vegetables. A comparison of data collected against WHO set limits for heavy metals in water for irrigation use and in vegetables for human consumption was done.

Data analysis also involved computation of soil to plant metal **transfer factor (TF)** using the equation;

$$TF = {}^{Csoil}/_{Cplant}$$

where C_{plant} is the concentration of heavy metals in plants and C_{soil} is the concentration of heavy metals in soil.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, the results of the study are presented and discussed with reference to the aim of the study which was to determine the physicochemical parameters and heavy metal concentration in two urban streams in water, soil and vegetables in two urban streams and those sold in Machakos municipality.

4.2 Point Source Water pollution

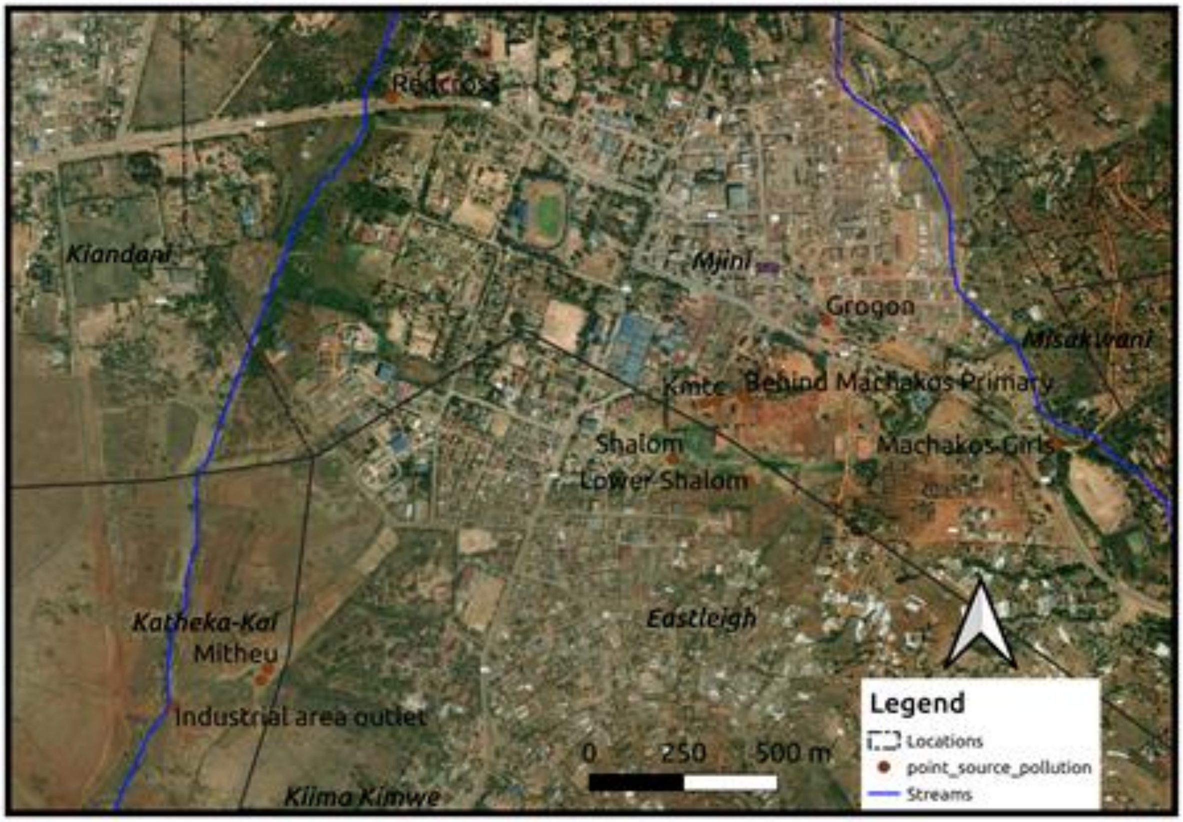

Figure 4.1: Point source water pollution in Machakos town

Figure 4.1 represents point sources of water pollution where raw sewage leaks into the environment and in some of the areas directly into the urban streams under study. Some of these point sources were, Machakos main open air garage (Grogon), behind Machakos primary, adjacent to Kenya Medical Training College (KMTC) wall, near Machakos Girls' and behind Shalom hospital. From the research, it was evident that sewage is contaminating the urban streams water by introducing both biological and chemical contaminants into the urban stream water.

4.3 Physicochemical Parameters

4.3.1 Water pH

pH is commonly known as the measure of acidity or alkalinity of water sources and can affect plant growth and plant health. The pH values obtained from this study varied slightly ranging from 7.5 to 8.45 (Table 4.3). The pH at site 1 (Mwanyani) ranged from 8.42 to 8.5 with mean pH of 8.45±0.04. Site 2 (Ikiwe – upstream) recorded a mean pH value of 7.50±0.20 with pH variations between 7.38 and 7.90. The mean pH value at site 3 (Ikiwe – downstream) was 7.91±0.10 with the pH values during the period of study ranging from 7.83 – 8.10. Site 1 recorded the highest mean pH value. Municipal sewage and domestic effluent from surrounding residential areas leaking into site 1 could be associated to the high pH at that site. Slightly alkaline pH values were obtained in all the water samples, hence not likely to cause health issues such as acidosis (Badr *et al*., 2020). The pH values were significantly different across the water sampling sites ($p \leq 0.05$). Values obtained in this study were within WHO pH recommended levels (6.5 – 8.5) for surface water hence suitable for agricultural use.

Similar pH values (7.0 – 8.9) were recorded in a previous research carried out in Cauvery river water (Begum *et al*., 2009). Additionally, reports of pH values (6.15 – 7.15) agreeable to those obtained in this study were made (Okoya *et al*., 2020). On the other hand, lower pH values (5.43-9.34) were recorded for Padma river, Bangladesh than pH values recorded in this study (Haque *et al*., 2019).

4.3.2 Water Temperature

Temperature of water is an important parameter which affects amount of dissolved oxygen in the water (Singh *et al*., 2016). Solubility of oxygen in water increases with decreasing temperature. Mean temperature values of water from the different sampling sites during the period of study ranged between 21.6 and 23.5 ºC (Table 4.3). The least mean temperature (21.58 ±3.47) was recorded at site 3 (Ikiwe – downstream) while the highest temperature mean (23.05 ± 2.59) was recorded at site 2 (Ikiwe - upstream). These temperature values majorly depend on the season of sampling and the time of sampling as the intensity of heat from the sun varies with season and time. The water temperature was within the ambient air temperature of the region and the sampling sites had temperature values within recommended and suitable range. One-way analysis of variance (ANOVA) showed no significant difference (p = 0.988) in river water temperature among the different sampling sites.

Temperature values reported in this study are in agreement with temperature values presented in past studies in Sagbama creek and Niger Delta, Nigeria (Seiyaboh *et al*., 2017). On the contrary, values recorded in this study were lower than those (24.00 - 29.32 and 20.17 – 32.2 ºC) in southwestern Nigeria and Bangladesh (Okoya *et al*., 2020; Haque *et al*., 2019).

4.3.3 Total Dissolved solids (TDS)

Total Dissolved Solids determine the amount of solid materials dissolved in the surface or ground water (Gupta *et al*., 2017). Synthetic organic chemicals present in water even in small concentrations impart distinct taste, color and odor to river water. Total dissolved solids (TDS) mean values from the sampling sites ranged from 577.5 to 865.8 mg/L (Table 4.3). During the period of study, site 1 (Mwanyani) recorded TDS values ranging between 682 – 944 mg/L with the mean value of TDS at that site being 865.83±116.78 mg/L. TDS values at site 2 (Ikiwe -upstream) varied from 445 to 890 mg/L. The mean TDS value for the sampling period at that site was 699.33±202.60 mg/L. Site 3 (Ikiwe - downstream) had a mean TDS value of 577.5±260.49 with TDS values ranging between 317 and 896 mg/L in the period of study. The highest TDS (865.83 ±116.7 mg/L) value recorded at site 1 reflects the impact of direct entry of raw sewage into Iini stream. Machakos open-air garage and car washes around Iini stream could be associated to the high TDS at site 1 since car battery acids, engine oils, salts, metallic wastes and other solid wastes are washed down into Iini stream. The lowest mean value of TDS was obtained at site 3 (Ikiwe-downstream) (577.5±260.49 mg/L). At site 3, there is much dilution of river water as Iini stream joins with other streams forming the larger Ikiwe river resulting to a lower TDS values at site 3. The TDS values obtained in the different sampling sites were within acceptable standards(WHO, 2008). There were no significant differences in TDS across the sampling sites ($p \leq 0.05$). Ewaid & Abed (2017) recorded TDS values (620 – 870 mg/L) which agree with TDS values recorded in this study. Contrarily, lower TDS values (108 – 234 and 176 – 438 mg/L) were reported for

Narmada River, India and Nairobi River respectively (Gupta *et al*., 2017; Mbui *et al*., 2016).

4.3.4 Electrical Conductivity (EC)

Electrical conductivity (EC) mean values in the sampling sites during the period of study varied between 864.8 and 1778.5 µs/cm. EC mean values at site 1 (Mwanyani) ranged between 1605 to 1844 µs/cm with the mean EC value at this site being 1778.5±102.17 µs/cm. An EC range from 754 to 1750 µs/cm was recorded at site 2 (Ikiwe-upstream) with EC mean value of this site at 1133.83±474.22 µs/cm. Site 3 (Ikiwe-downstream) recorded a mean of 864.83±216 µs/cm with the EC values varying between 620 and 1111 µs/cm during the period of study. Site 1 had the highest EC value. This may be associated to entry of both municipal and domestic effluents into the urban streams because the effluents contain dissolved salts. The study shows that there is a correlation between conductivity and total dissolved solids; at site 1 where electrical conductivity was highest, the value of total dissolved solids was also highest. This is an indication that the dissolved salts are responsible for the electrical conductivity of water. Electrical conductivity depends on concentration and mobility of ions. The higher the concentration of ions the higher the EC value and vice versa. Electrical conductivity is a good measure of dissolved solids hence an important criterion in determining quality of irrigation water (Choudhary *et al*., 2006). Comparable values ranging between 997 and 1082 µs/cm were reported by Ewaid & Abed (2017) in a study carried out in Al Gharraf River in southern Iraq. The EC values recorded in this study were slightly higher than those recorded in Nairobi River of 348-881 µs/cm respectively (Mbui *et al*., 2016). Choudhary *et al*.,

(2006) also recorded lower EC values for Kerwa, Kolar and Kaliasote manmade water reseviours.

Table 4.3: Mean ±standard deviation of physicochemical parameters of water

Site/Parameter	**Site 1**	**Site 2**	**Site 3**	**WHO Limits**	**p-value**
pH	8.45 ±0.04^a	7.50 ±0.20^b	7.91 ±0.10^c	6.5-8.5	0.000
Temperature (^{0}C)	22.05 ±1.29^a	23.05 ± 2.59^a	21.58 ±3.47^a	-	0.988
TDS (mg/L)	865.83 ±116.78^a	699.33 ± 202.60^a	577.5 ±260.49^a	1000	0.204
EC (µs/cm)	1778.5 ±102.17^a	1133.83 ±474.22^a	864.83 ± 216.83^a	700	0.305

Means with different superscripts (a, b, c) in the same row are significantly different at $p \leq 0.05$

4.4 Heavy Metal Concentration in Water

Heavy metal concentration (Cd, Cu, Pb, Zn and Cr) range in water from the different sampling sites were; 0.000033-0.0011, 0.0034-0.0055, 0.0012-0.007, 0.0232-0.1351, 0.0036-0.0292 mg/L respectively. All mean values were below WHO permissible limits for irrigation water in all the sampling sites (Table 4.4) hence the water was safe for agricultural use. The mean heavy metal concentration in water varied in the order Zn> Cr>Pb> Cu>Cd.

4.4.1 Cadmium

The concentration of Cd in water ranged from 0.000033 to 0.0011 mg/L with Cd having the lowest concentration in all the sampling sites. Cd concentration in site 1 varied between BDL – 0.0034 mg/L with a mean concentration of 0.0011±0.0014 mg/L. Site 2 (Ikiwe - upstream) had a mean Cd level of 0.0005±0.00096 mg/L with the levels ranging between BDL – 0.002 mg/L. The mean Cd concentration for site 3 (Ikiwe - downstream) was 0.000033±0.000058 mg/L with a range of BDL – 0.0001 mg/L. Site 1 (Mwanyani) had the highest mean concentration while site 3 (Ikiwe - downstream) had the least Cd mean concentration. At site 1, there was raw sewage released directly into Iini stream at this point. The sewage effluent could be containing cadmium compounds that could be responsible for Cd in water at site 1. Lower Cd concentrations downstream could be due to dilution of wastewater by river water.

Table 4.4: Mean ± standard deviations of heavy metal concentration (mg/L) in water and WHO set limits (WHO, 2008)

Heavy metals in water (mg/L)	**Site 1**	**Site2**	**Site 3**	**WHO Limit**	**p-value**
Cd	0.0011±0.0014	0.0005±0.00096	0.000033±0.000058	0.003	0.395
Cu	0.0055±0.0068	0.0037±0.0069	0.0034±0.0049	2.0	0.870
Pb	0.007±0.0110	0.0012±0.0024	0.0062±0.0055	0.01	0.417
Zn	0.1351±0.1236	0.0232±0.0352	0.0637±0.1026	3.0	0.210
Cr	0.0292±0.0505	0.0072±0.0158	0.0036±0.0063	0.05	0.494

The levels of Cd in water for all the different sampling sites were within WHO recommended limits for surface water hence the water was safe for agricultural use. There was no significant difference ($p>0.05$) in Cd concentration in the different sampling sites. These values were lower than Cd concentrations (0.0043 mg/L) detected in Nairobi River and 0.007 – 0.16 mg/L recorded for wastewater in Embu (Sayo *et al*., 2020; Njuguna *et al*., 2017). Contrary to Cd levels obtained in this study, Mohsin *et al*., (2019) reported higher Cd concentration (0.02 – 0.39 mg/L).

4.4.2 Copper

The average Cu concentration in the different sampling sites ranged from 0.0034 to 0.0055 mg/L with the highest value recorded at site 1. Variation of Cu concentration in the sampling site was; BDL – 0.0074 mg/L for site 1, BDL – 0.0159 mg/L for site 2 and BDL – 0.009 mg/L for site 3. Discharges from industries and sewage treatment plants and natural weathering of rocks are some pathways through which copper is released to water (Nzeve *et al*., 2015). The high level of copper at site 1 could be attributed to raw sewage effluent at site 1, pesticides and fertilizers that leached into the water from the surrounding farms and erosion of minerals from rocks and soil. Generally, the concentration of Cu was within the recommended level of Cu in surface water (WHO, 2008). The Cu levels in the different sampling sites showed no significant variation ($p>0.05$). The levels of Cu were lower than previous levels (1.29-0.727 mg/L) determined in river Chawalla, Nigeria (Bichi *et al*., 2010). Kacholi (2018) also reported higher Cu values than those obtained in this study for urban stream water in Dar es Salaam, Tanzania.

4.4.3 Lead

The mean Pb concentrations varied between 0.0012 and 0.007 mg/L (Table 4.4). Pb concentration in water samples from site 1 (Mwanyani) varied from BDL to 0.2336 mg/L with a mean Pb concentration of 0.007±0.0110 mg/L recorded for the period of study. Site 2 (Ikiwe upstream) recorded a minimum Pb concentration of BDL and a maximum of 0.0823 mg/L. The average Pb concentration at site 2 was 0.0012±0.0024 mg/L while Pb concentration in water samples from site 3 (Ikiwe downstream) ranged from BDL to 0.1820 mg/L with a mean value of 0.0062±0.0055 mg/L. Highest Pb levels were noted in site 1 while the lowest levels in site 2. Lead in water samples from site 1 could be coming from; petroleum products and metallic waste from Machakos open air garage located next to Iini stream, sewage effluent released directly into the stream and airborne Pb deposition. Concentration of lead in all the sampling sites was within acceptable Pb levels in river water hence there was no Pb pollution presently. The Pb in the different sampling sites did not show any significant variation ($p > 0.05$).

A similar studies carried out in previous studies recorded higher values than those obtained in this study; 0 – 0.158 mg/L reported for Nairobi River, Kenya (Njuguna *et al*., 2017), mean Pb value of 8.60 mg/L reported in Riyadh city river waters (Badr *et al*., 2020) and 0.113 mg/L of Pb was reported from Yucuambi river (Villa *et al*., 2018). Xiao *et al*., (2019) reported 0.25 mg/L-0.25 mg/L while Kacholi (2018) recorded 0.46 - 0.55 mg/L from Temeke, Dar es Salaam.

4.4.4 Zinc

Concentration of zinc in water in the sampling sites was found to be in the range 0.0232 to 0.1351 mg/L and was found to be the highest among the heavy metals investigated. Zn had the highest concentration of 0.1351 mg/L at site 1 where raw sewage drains into Iini stream thus explaining the high level of zinc at that site since the raw sewage contains dissolved zinc compounds. Lowest Zn levels (0.0232 mg/L) were recorded at site 2 (Ikiwe upstream). On the other hand, average Zn mean of 0.0637 mg/L was recorded in water samples from site 3 (Ikiwe downstream). Erosion of minerals from rocks and soil could also be another natural pathway of introduction of zinc in river water (Saskatchewan, 2007). Additionally, other sources of Zinc could be steel products, burning of waste materials, leaching of fertilizers and pesticides into the water. Zn in water samples from all the sampling sites was within acceptable WHO limits. This was an indication that the water was not zinc polluted. There was no significant variation in concentration of Zn in the sampling sites ($p > 0.05$).

Ahmed *et al*., (2018) in a similar study in Bangladesh also reported Zn out of the six heavy metals assessed as having the highest concentration. Comparable mean Zn values in surface water were reported in previous studies; 0.092 – 0.132 mg/L were reported in study carried out in Masinga dam, Kenya (Nzeve *et al.,* 2015). 0.99 – 1.26 mg/L obtained in Temeke municipality in Dar es Salaam (Kacholi, 2018). 0.34 – 1.85 mg/L detected in Sahiwal district, Pakistan (Mohsin *et al*., 2019). Contrarily, the values of Zn (2.0 – 13.7 mg/L) reported in Bangladesh were higher compared to Zn level values obtained in this study (Ahmed *et al*., 2018).

4.4.5 Chromium

The concentration of chromium ranged from 0.0036 to 0.0292 mg/L (Table 4.4). Cr levels at site 1 (Mwanyani) ranged from BDL to 0.1187 mg/L with an average mean of 0.0292±0.0505 mg/L. At site 2 (Ikiwe upstream) the mean Cr concentration was

0.0072±0.0158 mg/L with Cr levels varying between BDL and 0.0355 mg/L during the period of study. Cr range at site 3 (Ikiwe downstream) was BDL – 0.0109 mg/L while the average mean was 0.0036 ± 0.0063 mg/L at that site. The highest mean concentration of chromium was at site 1. This could be associated to raw sewage drained into Iini stream at site 1 as the sewage could contain dissolved chromium compounds from paints. Additionally, washing of motor bikes in Iini stream could also be attributed to Cr in water as some motorbikes have chrome plating and the Cr gets deposited in the water (Njuguna *et al*., 2017). One-way ANOVA showed there was no significant variation ($p > 0.05$) in Cr concentration in the different sampling sites. Concentration of Cr in the water from all the sampling sites was lower than WHO acceptable standards for irrigation water, hence not polluted with chromium.

Similar values (0 – 0.32 mg/L) to those obtained in this study were recorded in Cauvery River (Begum *et al*., 2009). Cr mean concentrations obtained in this study were lower than those recorded in previous studies; Njuguna *et al*., (2017) reported 0.245 mg/L in Nairobi river, Xiao *et al*., (2019) reported 5.13 mg/L in river water in Chinese Loess Plateau and Woldetsadik *et al*., (2017) detected 2.26 – 6.76 mg/L in Tinishu and Teleku Akaki rivers in Addis Ababa.

4.5 Heavy Metal Concentration in Soil

Heavy metal mean concentration values determined during the period of study are reported in Table 4.5. The concentrations were all below WHO set limits for heavy metals in agricultural soil for all the sampling sites. However, the levels of Cd, Pb, Zn, Cu and Cr observed in soil were elevated compared to concentration in water. This could be due to continous irrigation of the agricultural farms using polluted water.

4.5.1 Cadmium

The mean values for Cd ranged from 0.0058±0.0101 to 0.0534±0.0419 mg/kg as indicated in Table 4.5. At site 1 (Mwanyani), Cd range was BDL – 0.1042 mg/kg, with the mean concentration at that site being 0.0534±0.0419 mg/kg. Site 2 (Ikiwe upstream) had a lower Cd mean concentration (0.0072±0.0161 mg/kg) with the minimum and maximum Cd concentration during the period of study for this site recorded as 0.000 and 0.0360 mg/kg respectively. Site 3 (Ikiwe downstream) had the lowest Cd concentration (0.0058±0.0101 mg/kg). Cd levels at site 3 ranged between BDL and 0.0174 mg/kg during the period of study. Cd levels in all the sampling sites were lower than WHO acceptable standards for Cd in agricultural soil implying that the soil at that time was not Cd contaminated. There was no significant difference of heavy metals' concentration in the different sampling sites (p value was greater than 0.05).

Table 4.5: Mean ± Standard deviations of heavy metal mean concentration in soil (mg/kg) and WHO set guidelines

Heavy metals in soil (mg/kg)	Site 1	Site 2	Site 3	WHO Limit	p-value
Cd	0.0534±0.0419	0.0072±0.0161	0.0058±0.0101	3	0.051
Cu	10.39±4.72	27.4±43.0	27.5±27.7	100	0.624
Pb	7.56±5.59	8.35±5.91	4.23±3.71	84	0.581
Zn	28.0±31.7	28.8±23.9	20.1±19.4	300	0.894
Cr	10.03±6.02	9.99±4.95	8.17±5.92	30	0.319

Cd in soil could be originating from sewage and domestic effluents, organic matter, phosphate fertilizers, mineralization and atmospheric deposition (Abraham, 2020; Birke *et al*., 2017).

Compared with the current study similar Cd levels, were reported in previous studies; 0.45 mg/kg in New Zealand, 0.185 mg/kg in Europe and 0.11 mg/kg in Switzerland agricultural soils (Abraham, 2020; Birke *et al*., 2017; Bigalke *et al*., 2017). However, a higher level of Cd (7.13 – 11.13 mg/kg) was found in western region of Saudi Arabia in wastewater irrigated soil (Balkhair & Ashraf, 2016)

4.5.2 Copper

The level of Cu in soil in this study ranged between 10.39 and 27.5 mg/kg. Range of Cu concentration in the sampling sites in the period of study were as follows; 3.907 – 16.64 mg/kg in site 1 (Mwanyani), 0.00 – 103.857 mg/kg in site 2 (Ikiwe upstream) and 0.00 – 55.47 mg/kg in site 3 (Ikiwe downstream). All the values were found to be lower than WHO accepted standards of Cu in soil thus the soil was not copper polluted. There was no significant difference ($p > 0.05$) in the concentration of Cu in the sampling sites. Application of sewage on agricultural soil, fungicides and pesticides used during farming and atmospheric deposition could be associated to the presence of Cu in soil (Panagos *et al*., 2018).

Similar Cu levels to those detected in this study were reported in previous studies; 16.7 mg/kg for European agricultural soils (Panagos *et al*., 2018) and 28.74 mg/kg for waste water irrigated soils in Lahore, Pakistan (Mahmood & Malik, 2014). Values for Cu in soil (40.961 mg/kg) noted in Yangtze River Delta were higher than the values of Cu in soil obtained in this study (Mao *et al*., 2019). Contrarily, lower Cu levels were detected in previous studies on concentration of Cu in cropland soils; 1.33 – 3.33 mg/kg in Kericho West sub county and 1.661 – 3.781 mg/kg in Embu, Kenya (Sayo *et al*., 2020; Bett *et al*., 2019).

4.5.3 Lead

Concentration mean values of Pb were between 4.23±3.71 and7.56±5.59 mg/kg as shown in Table 4.5. Pb levels ranged from 0.00 to 15.47 mg/kg, 0.00 to 15.6 and 0.00 to 6.9398 mg/kg at site 1 (Mwanyani), site 2 (Ikiwe upstream) and site 3 (Ikiwe downstream) respectively. Highest mean Pb levels were at site 2 and the lowest at site 3. All Pb values were within WHO permissible limits for agricultural soils in the different sampling sites. There was no significant variation in the Pb levels in the different sampling points ($p > 0.05$).

Similar results were reported by Bett *et al*., (2019) who recorded 5.00 ± 0.58 to 5.67 ± 0.88 mg/kg of Pb in soil in Kericho West sub-county, Kenya. Lower mean concentrations of Pb were reported in soil irrigated with sewage contaminated water in western region of Saudi Arabia (0.3 mg/kg), 0.034 - 0.985 mg/kg in Embu and 0.25 – 0.7 mg/kg along Lihe River, Tahiu (Sayo *et al*., 2020; Chen *et al*., 2018; Balkhair & Ashraf, 2016). On the other hand, Ikenaka *et al*., (2014) reported higher values (5 – 7.76 mg/kg) than those obtained in this study.

4.5.3 Zinc

Zinc generally had the highest mean values in the soil samples (20.1 – 28.8 mg/kg) in the different sampling sites. Zn levels at Site 1 (Mwanyani) ranged between 0.00 to 64.17

mg/kg. Variation of Zn at site 2 (Ikiwe upstream) was 0.00 to 63.01 mg/kg while at site 3 (Ikiwe downstream) the variation was 0.00 to 38.7572 mg/kg. Highest Zn concentration was at site 2 and the lowest at site 3. The mean concentration of Zn from all the sampling sites was below permissible standard set by WHO for agricultural soils. One - way analysis of variance (ANOVA) showed that there was no significant variation in Zn levels in the different sampling points ($p > 0.05$). Zn in soil could be associated to fertilizers and pesticides used in the farm fields, naturally occuring in rocks in the soil and heavy metals in the wastewater used to irrigate the farms.

The results in this study can be compared to those reported in previous studies which were below FAO/WHO permissible limits; Sayo *et al*., (2020) reported Zn levels lower than those detected in this study (3.011 – 4.679 mg/kg) in Embu, Kenya for wastewater irrigated soils while Woldetsadik *et al*., (2017) reported higher values (119 – 203mg/kg) than those obtained in this study from vegetable farming sites in Adddis Ababa

4.5.5 Chromium

Concentration of Cr in the study area ranged from 8.17±5.92 to 10.03±6.02 mg/kg as indicated in Table 4.5. The concentration of Cr during the period of study ranged as follows; 0.00 - 15.47, 0.00 – 34.753 and 4.465– 14.9982 mg/kg in site 1 (Mwanyani), site 2 (Ikiwe upstream) and site 3 (Ikiwe downstream) respectively. The highest Cr mean concentration (10.03 mg/kg) was recorded at site 1 with site 3 recording the lowest Cr mean concentration (8.17 mg/kg). All Cr values were within WHO recommended levels hence the soil in the sampling sites was safe for agricultural use. Chromium in the different sampling sites had no significant difference ($p>0.05$). Cr in soil could be originating from the sewage contamination of irrigation water, atmospheric emissions, and industrial effluents (Toxicology & Medicine, 2011)

These values are lower compared to Cr levels detected in previous studies; 30.67 -172.75 mg/kg for wastewater irrigated soils in suburban areas of Varanasi India (Kumar *et al*., 2007), 47.0 mg/kg in Mitidja plain, Algeria and 17–39 mg/kg at Kafue River, Zambia (Ikenaka *et al*., 2014). Khan *et al*., (2019) however reported higher Cr concentration in soils (0.9 – 1.8 mg/kg) than those obtained in this study.

4.6 Heavy Metal Concentration in Vegetables

4.6.1 Heavy Metal Concentration in Spinach and Kales Grown in the Urban Farms

Environmental contamination through various sources such as wastewater irrigation, air deposition and spillage have been termed as routes for heavy metals into vegetables and plants (Adedokun *et al*., 2016). The mean concentration results of Cd, Cu, Pb, Zn and Cr in the sampling sites for kales and spinach during the period of study are presented in Table 4.6.1. The heavy metal mean concentrations for Cd, Cu, Pb, Zn and Cr in the different sampling sites were 0.091, 1.933, 0.214, 15.337 and 0.842 mg/kg for kales respectively and 0.049, 7.453, 0.5127, 10.517 and 0.473 mg/kg respectively for spinach.

4.6.1.1 Cadmium

Concentration of Cd in spinach ranged from 0.00 to 0.1285±0.1291 while in kales the range was from 0.0040±0.0089 to 0.243±0.334 mg/kg in the different sites during the period of study. Cd level in spinach was highest (0.1285 mg/kg) in site 3 (Ikiwe downstream) and highest (0.243 mg/kg) in site 1 (Mwanyani) for kales. The study indicated that Cd in vegetables was within WHO/CODEX safe limits except Cd level in kales in site 1 (Stan, 2009). This was an indication that kales from site 1 were contaminated with Cadmium. Cadmium has been said to have a long biological half-life in humans (10 – 35 years) and is known to accumulate in the kidneys (Lee *et al*., 2012). The high level of Cd in site 1 was attributed to the raw sewage emitted directly into site 1 and is used for irrigating the crops. Cd could also be emanating from fertilizers used in farming the vegetables and air deposition of Cd. No significant variation in Cd levels in the different sampling sites was observed ($p > 0.05$).

The results obtained in this study are comparable to those obtained for Cd (0.0017 mg/kg) in Zhejiang, China (Pan *et al*., 2016), 0.13 mg/kg in Sao Paoulo state, Brazil (Guerra *et al*., 2012) and 0.021 – 0.171 mg/kg for wastewater irrigated spinach and kales in Embu Kenya. However Cd concentration detected in this study were lower than those reported for Cd in spinach (0.9 – 71.7 mg/kg) in Kericho, Kenya (Bett *et al*., 2019).

4.6.1.2 Copper

The concentration of Cu in spinach ranged between 3.07±3.65 and 14.5±11.55 mg/kg in the three sampling sites. Kales on the other hand had Cu levels ranging from 0.909±1.574 to 3.60±3.74 mg/kg. Cu concentration was highest in site 2 for both spinach and kales. The mean concentrations of Cu observed were within WHO permissible limits for both kales and spinach except Cu in spinach in site 2. Cu in wastewater used to irrigate the spinach, pesticides and fertilizers could explain the high concentration of Cu in spinach at site 2. Copper is an essential nutrient and plays a key role in enzymatic processes and in the synthesis of hemoglobin (Nzeve & Kitur, 2019). However, high levels of copper when ingested have been reported to have gastrointestinal effects in the human body (Lee *et al*., 2012). Cu concentration levels among the different sampling sites showed no significant difference (p> 0.05>).

Cu levels presented in this study are similar to Cu levels in vegetables reported in previous studies; 4.08 – 13.9 mg/kg were presented in a study carried out in Lagos, Nigeria (Adedokun *et al*., 2016) and 4.3 – 9.718 mg/kg reported for vegetables in Bangladesh (Shaheen *et al*., 2016). Contrary to values presented in this study, lower Cu concentrations were reported in other studies; (1.372 – 4.084 mg/kg) in spinach and kales irrigated with wastewater (Sayo *et al*., 2020) and 0.45 – 2.22 mg/kg in Banat county, Romania (Harmanescu *et al*., 2011). Higher Cu levels (14.0 – 62.7 mg/kg) were reported in Kericho West sub county (Bett *et al*., 2019) and 30.64 mg/kg in Varanasi, India (Sharma *et al*., 2008).

4.6.1.3 Lead

Concentration of Pb in spinach varied from 0.28±0.625 to 0.636±0.933 mg/kg in the three sampling sites while that of kales ranged between 0.00 and 0.458±0.517 mg/kg. The mean level of Pb in kales (0.214 mg/kg) was within WHO recommended limits (0.3 mg/kg) for kales but the mean concentration of Pb in spinach (0.513 mg/kg) exceeded WHO permissible limits. Spinach from site 1 (Mwanyani) and site 3 (Ikiwe downstream) and kales from site 3 exceeded WHO set standards for Pb in leafy vegetables (Stan, 2009). This was an indication that kales and spinach from those sites were not safe for human consumption and had health risks to the consumers.

High levels of Pb have been reported to have harmful effects resulting in biochemical defects of some body organs such as the liver, kidney, lungs and the neurological system

(Guerra *et al.*, 2012). The high Pb values could be due to the sewage water used to irrigate the vegetables, air deposition and petroleum products. Generally, Pb contamination in vegetables can be through sewage application, airborne deposition of Pb in highway traffic or due to contaminated soil. One Way analysis of Variance (ANOVA) showed no significant variation of Pb in the sampling sites.

Table 4.6.1: Mean ± Standard deviations of heavy metal mean concentration in vegetable (spinach and kales) (mg/kg) and WHO set guidelines

Heavy metals in spinach (mg/kg)	**Site 1**	**Site 2**	**Site 3**	**WHO Limit**	**p-value**
Cd	BDL	0.0197±0.0440	0.1285±0.1291	0.20	0.154
Cu	4.79±6.77	14.5±11.55	3.07±3.65	10.00	0.063
Pb	0.622±0.880	0.28±0.625	0.636±0.933	0.30	0.547
Zn	11.80±16.70	9.05±9.11	10.7±18.6	5.00	0.786
Cr	BDL	1.002±2.185	0.416±0.495	0.300	0.432
Heavy metals in kales (mg/kg)	**Site 1**	**Site 2**	**Site 3**	**WHO Limit**	**p- value**
Cd	0.243±0.334	0.0040±0.0089	0.0250±0.0433	0.20	0.038
Cu	1.29±1.820	3.60±3.74	0.909±1.574	10.00	0.336
Pb	BDL	0.184±0.273	0.458±0.517	0.300	0.868
Zn	12.06±11.90	15.15±10.08	18.8±32.6	5.00	0.835
Cr	BDL	0.906±1.354	1.62±2.8	0.30	0.411

Compared to other studies, higher concentrations of Pb (5.44mg/kg) were recorded in a previous study in leafy vegetables in Lagos, Nigeria (Adedokun *et al*., 2016). Mohsin *et al*., (2019) also reported higher values of Pb in spinach (2.28 mg/kg) in Sahiwal district, Pakistan. On the other hand, Shi *et al*., (2020) reported lower Pb levels (0.0464 mg/kg) in polluted areas of China.

4.6.1.4 Zinc

Zinc was the most abundant of all the five heavy metals in the sampling sites. Concentration of Zn in spinach ranged between 9.05±9.11 and 11.80±16.70 mg/kg while that of kales was 12.06±11.90 and 18.8±32.4 mg/kg. Site 1 (Mwanyani) had the highest Zn concentration in spinach while site 3 (Ikiwe downstream) had the highest concentration of Zn in kales. Concentration level of Zn in all the sampling sites was slightly higher than the permissible limits of Zn in vegetables recommended by World Health Organization. Zn is necessary as an essential element in the human nutrition to sustain the functioning of the immune system hence it is actively taken up by plants. However, high levels of zinc are associated with nausea, diarrhea vomiting, hematological effects and gastrointestinal (Wei *et al*., 2019).

Similar values of Zn were recorded (12.5 – 18.55 mg/kg) in a previous study carried out in Yola and Kano for vegetables (Chiroma & Ebewele, 2014). Hussain *et al*., (2019) reported lower Zn values (0.213 – 0.327 mg/kg) than those detected in this study.

4.6.1.5 Chromium

Chromium mean concentrations in sampled spinach vegetables ranged between 0.00 and 1.002±2.185 mg/kg and 0.00 to 1.62±2.8 mg/kg for kales in the three sampling sites.

Highest Cr concentration in spinach was observed at site 2 (Ikiwe upstream) while highest Cr concentration in kales was noted at site 3 (Ikiwe downstream). One – way ANOVA did not show any significant difference in Cr concentration in the various sites. Mean Cr levels in both spinach and kales at site 2 and site 3 exceeded WHO recommended limits (0.3 mg/kg) for human consumption indicating that the spinach and kales from these sites were unsafe for human consumption with respect to Cr. However, Cr levels in spinach and kales from site 1 were below detectable limit (BDL) thus not contaminated with Cr. Chromium is an essential dietary nutrient in low doses required to potentiate insulin and normal glucose metabolism (Toxicology & Medicine, 2011). However, exposure to higher concentrations of Cr are said to have carcinogenic, renal, hepatic, gastrointestinal, cardiovascular and hematological effects (Toxicology & Medicine, 2011). Chromium in the vegetables could be emanating from contaminated water and soil, air deposition and naturally occurring in soil and rocks.

Pan *et al*., (2016) recorded similar values (0.2 – 1.51 mg/kg) of Cr in leafy vegetables to the values detected in this study. Mean Cr levels in this study compared well to Cr values (0.27 mg/kg) reported in Sao Paulo State (Guerra *et al*., 2012). Additionally, Balkhair & Ashraf, (2016) also reported similar Cr levels (1.85 mg/kg) in vegetables in Saudi Arabia. Lower Cr concentration in spinach (0.092 – 0.36) were reported by Hussain *et al*., (2019) compared to those detected in this study.

4.6.2 Heavy Metal Concentration in Kales and Spinach Sold in the Market Sites

Heavy metal concentration levels in spinach and kales collected from the urban market sites are presented in Table 4.6.2 and Table 4.6.2 1.

4.6.2.1 Cadmium

Cadmium metal has a high mobility and can be easily transported from the soils and absorbed into the different parts of the plant (Heshmati *et al*., 2020). The means and standard deviations of Cd concentration in the kale samples from the three urban market-sampling sites are presented in table 4.6.2. The highest Cd concentration recorded for the market sites was 0.113±0.106 mg/kg while the lowest was 0.00. The mean concentration of Cd in kales in the market sites varied in the order Supermarket 1 (SPM 1) > Supermarket 2 (SPM 2) > Open-air market. The level of Cd in spinach ranged between 0.055±0.081 and 0.172±0.178 mg/kg. Kale samples from SPM 1 recorded the highest Cd mean concentration. All Cd concentration values in spinach and kales were within 0.2 mg/kg WHO set limit (Stan, 2009). This implied that the kales and spinach sold in the market sites were not contaminated with Cd hence were safe for human consumption. Cd in vegetables was attributed to different sources such as agricultural fertilizers, pollutants in irrigation water and atmospheric deposition.

Values of Cd (0.108 mg/kg) reported for a study in western Iran agree with the levels recorded in this study (Heshmati *et al*., 2020). Lower Cd values (3.89±0.17 – 4.13±0.14 mg/kg) than those obtained in this study were recorded for vegetables in Saudi Arabian markets (Ali & Al-Qahtani, 2012). However, values recorded in this study are higher compared to those reported by Alimohammadi *et al*., (2018) for Tehran supermarket vegetable samples.

4.6.2.2 Copper

The results of copper concentration in kale and spinach vegetables in the different sampling sites are presented in table 4.6.2 and table 4.6.2.1. The level of copper in kales from the market sites ranged between 0.971±0.894 and 1.706±1.474 mg/kg. The mean concentration of Cu in spinach varied between 3.923±2.158 and 4.93±2.97 mg/kg. The values of Cu in both kales and spinach were within WHO accepted limits hence the kales and spinach sold in the market sites had no copper health hazard exposure to the consumers.

Values recorded in this study agree to values reported in previous studies; 0.041 – 0.829 mg/kg for vegetables in Tehran supermarkets (Alimohammadi *et al*., 2018) and 2.39 – 10.19 mg/kg in Lagos metropolis, Nigeria for vegetables in different markets (Adedokun *et al*., 2016). Ali & Al-Qahtani, (2012) on the one hand reported higher concentration of Cu in spinach (11.38 – 14.07 mg/kg) in Saudi Arabian markets.

Table 4.6.2: Mean ± standard deviation of heavy metal concentration (mg/kg) in kale (market sites) and WHO recommended levels

Sampling Site		**Mean ±StDev (mg/Kg)**				
	N	Cadmium (Cd)	Copper (Cu)	Lead (Pb)	Zinc (Zn)	Chromium (Cr)
SPM 1	4	0.113±0.106	1.706±1.474	0.331±0.572	17.86±18.13	0.112±0.250
SPM 2	4	0.013±0.026	0.971±1.400	0.236±0.439	26.7±24.00	14.0±26.90
OAM	4	BDL	0.971±0.894	0.156±0.191	11.06±11.34	0.280±0.561
WHO Set		0.2	10.0	0.3	5.0	0.3
P-value		0.391	0.571	0.577	0.934	0.497

*SPM – supermarket, *OAM – open-air market, *WHO – world health organization

4.6.2.3 Lead

Table 4.6.2 shows the mean concentration of Pb in kales from the three sampling points while the mean concentrations in spinach are presented in table 4.6.2.1. The concentration of lead ranged from 0.156±0.191 to 0.331±0.572 mg/kg and from 0.098±0.2191 to 0.867±1.158 mg/kg for kales and spinach from the market sites respectively. The mean concentration of Pb in kales from SPM1 exceeded WHO safe limit for Pb in leafy vegetables while mean Pb concentration in kales from SPM 2 and the open air market (OAM) was within WHO permissible limit. It is thus deducible that kale from SPM 1 were exposing consumers to unsafe Pb levels hence the kale from SPM 1 was not safe for consumption. The level of Pb in spinach from open-air market and SPM 1 the exceeded WHO recommended limits while Pb in spinach from SPM 2 was within WHO safe Pb limit in vegetables. Based on these findings, spinach from the open-air market and SPM 1 had health risk implications to the consumers. Pb in the vegetables could be from varied sources such as petroleum products, use of wastewater to irrigate the vegetables and automobile emissions.

Similar Pb values (0.072-0.289 mg/kg) were reported in a study on heavy metal concentration in vegetables in local market of Jordan (Osaili *et al.*, 2016). On the other hand, a study in western Iran recorded lower Pb values (0.022 – 0.04 mg/kg) which were within WHO recommended levels.

4.6.2.4 Zinc

Zn in vegetables ranged from 11.06±11.34 to 26.7±24.00 mg/kg and from 12.14±11.31 to 20.7±24.7 mg/kg for kales and spinach respectively from the market sites. Zn concentration in both spinach and kale from all the sampling sites was higher than WHO recommended limit and thus the vegetables from the market sites were likely to have harmful health effects due to high Zn levels in the vegetables. Zinc is an essential trace element of great importance in the human dietary nutrition and health and is thus known to be the most abundant trace metal in the human body after iron (Wong *et al*., 2019). Findings from this study showed lower zinc levels when compared with those recorded in a previous study (23.8 – 89.8 mg/kg) carried out in Maun market, Botswana (Bati *et al*., 2016).

Table 4.6.2.1: Mean ± standard deviation of heavy metal concentration (mg/kg) in spinach (market sites) and WHO limits

Sampling Site	N	**Mean ±StDev (mg/Kg)**				
		Cadmium (Cd)	**Copper (Cu)**	**Lead (Pb)**	**Zinc (Zn)**	**Chromium (Cr)**
SPM 1	4	0.172±0.178	4.70±4.41	0.439±0.511	20.7±24.7	4.43±9.72
SPM 2	4	0.055±0.081	4.93±2.97	0.098±0.219	12.14±11.31	1.80±3.87
OAM	4	0.106±0.085	3.923±2.158	0.867±1.158	17.94±15.49	4.24±8.90
WHO Set		0.2	10.0	0.3	5.0	0.3
p-value		0.469	0.229	0.773	0.923	0.908

*SPM – supermarket, *OAM – open-air market, *WHO – world health organization

4.6.2.5 Chromium

Concentrations of Cr in kales and spinach are shown in table 4.6.2 and 4.6.2.1 respectively during the period of study. Vegetable samples from the market sites showed varying Cr concentrations; 0.112±0.25 – 14.0±26.9 mg/kg for kales and 1.80±3.87 – 4.43±9.72 mg/kg for spinach. This study revealed that kales from SPM 2 and spinach from OAM and SPM 1 had accumulated Cr higher than the accepted level. The concentration was very high in samples from SPM 2 (14.0 mg/kg). This study shows that kales and spinach from sampling sites, which exceeded the permissible Cr limits, were not safe for human intake. The results obtained showed similar Cr levels in the vegetables compared to those recorded by Pan *et al*., (2016) and Osaili *et al*., (2016) who also detected that Cr concentration (0.057 – 3.51 mg/kg) was exceeding the recommended worldwide standards.

4.7 Pearson Correlation Analysis of Heavy Metals in Water, Soil and Vegetables

A general Pearson correlation analysis of the relationship between heavy metal concentrations in water, soil and vegetables is presented in a matrix plot in Figure 4.2. Additionally, the relationship between heavy metal variables in water, soil and vegetables is presented in Pearson correlation analysis table in Table 4.7.

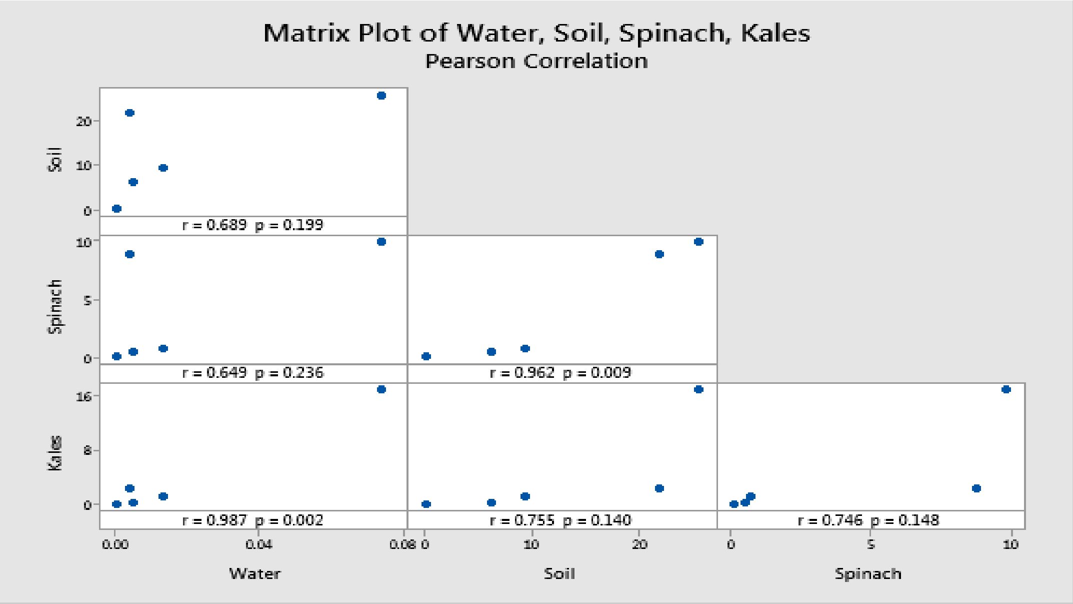

Figure 4.2: Pearson correlation matrix plot for heavy metals in water, soil, spinach and kales

Heavy metal levels in water and those in soil showed a positive correlation (r = 0.689; p = 0.188). Positive correlation was also observed for the concentration of heavy metals in water and with the concentration in spinach (r = 0.649; p = 0.236). Significant positive correlation was observed between the concentration of heavy metals in kale and those in water (r = 0.987; p = 0.002) and concentration of metals in soil and those in the spinach (r = 0.962; p = 0.009). Pearson correlation analysis indicated positive correlation between the concentration of heavy metals in soil and the concentration in kales (r = 0.755; p = 0.140). The level of heavy metals in spinach and that in kale (r = 0.746; p = 0.148) were observed to have a positive correlation.

Positive correlation was also observed between the concentration of heavy metals in vegetables and concentration in soil in a study carried out in Varanasi, India (Kumar *et al.*, 2007). Heavy metals that showed a considerable positive correlation are likely to have identical properties, have a similar source, were influenced by related elements or could be mutually dependent (Oghenebrorie & Chudy, 2020; Makokha *et al.*, 2016).

Correlation between heavy metal concentration may suggest identical heavy metal accumulation properties in water, soil or vegetables (Xu *et al.*, 2013). In addition, physical and chemical processes occurring in the environment could also influence correlation of the heavy metals.

Table 4.7: Pearson Correlation matrix coefficients for heavy metals in soil, water, spinach and kales

	Cd water	**Cu Water**	**Pb Water**	**Zn Water**	**Cr Water**	**Cd Soil**	**Cu Soil**	**Pb Soil**	**Zn Soil**	**Cr Soil**
Cd water	1									
Cu Water	0.385	1								
Pb Water	-0.153	0.319	1							
Zn Water	0.374	**0.561***	**0.678****	1						
Cr Water	0.173	0.022	**0.774****	0.538*	1					
Cd Soil	0.201	-0.064	0.355	0.337	0.446	1				
Cu Soil	-0.189	-0.173	-0.014	-0.139	-0.108	-0.269	1			
Pb Soil	0.250	0.084	0.027	0.325	0.156	-0.181	.258	1		
Zn Soil	0.185	0.458	0.047	0.465	-0.159	-0.077	.030	**0.668****	1	
Cr Soil	0.067	0.043	0.014	-0.035	0.037	-0.238	**0.808****	0.247	-0.069	1
Cd Spinach	-0.200	0.375	0.409	0.511	0.113	0.170	-0.323	-0.304	0.382	-0.199
Cu Spinach	0.037	0.378	0.383	0.574	0.054	-0.367	0.270	0.448	0.518	0.160
Pb Spinach	-0.096	0.620*	**0.694***	**0.741****	0.246	0.203	-0.148	0.052	**0.737****	-0.016
Zn Spinach	-0.101	**0.693***	**0.721***	**0.795****	0.110	0.131	-0.118	0.086	**0.744****	0.039
Cr_Spinach	0.053	0.081	0.255	0.410	-0.262	0.404	-0.110	-0.320	0.056	-0.366
Cd_Kales	-0.166	-0.116	-0.166	-0.103	-0.155	-0.142	-0.281	-0.414	-0.266	-0.320
Cu_Kales	0.498	**0.707***	0.200	0.408	-0.318	-0.300	0.122	0.126	0.381	0.285
Pb_Kales	-0.106	0.631	**0.711***	**0.739***	0.280	0.195	-0.151	0.062	**0.744***	-0.029
Zn_Kales	-0.113	**0.726***	**0.804****	**0.931****	0.174	0.027	-0.118	0.159	**0.849****	-0.037

Cr_Kales	-0.317	-0.231	0.207	-0.174	-0.041	-0.292	0.157	-0.198	-0.166	-0.096

- Bold * - positive correlation significant at the 0.05 level. Bold** - positive correlation significant at the 0.01 level

4.8 Transfer Factor of Heavy Metals in Vegetables

The transfer factor (TF) signifies the amount of heavy metal in the soil which is transferred to the vegetable crops. Transfer factor (TF) is one of the key components of human exposure to heavy metals through the food chain. Transfer factor mean values in kales were 4.103, 0.088, 0.032, 0.598 and 0.090 respectively while in spinach for Cd, Cu, Pb, Zn and Cr were 2.235, 0.340, 0.076, 0.410 and 0.050 respectively (Table 4.8). The transfer factor trends in ranking order were Cd>Zn>Cu>Pb>Cr in Spinach and Cd>Zn>Cr>Cu>Pb in Kale.

Table 4.8: Mean Transfer factor of heavy metals from soil to plants

Heavy metal	**Cd**	**Cu**	**Pb**	**Zn**	**Cr**
TF in Spinach	2.235	0.340	0.076	0.410	0.050
TF in Kales	4.103	0.088	0.032	0.598	0.090

The highest transfer factor in spinach was by Cd (2.235) implying high absorption and accumulation of the metal by spinach. On the other hand, Cr had the lowest transfer factor in spinach (0.050). Cd also had the highest TF in kale (4.103) with Pb having the least TF in kales (0.032). From the findings, it is clear that vegetables are accumulating heavy metals from the soil where they are planted. Our study is in agreement with previous findings of TF reported in an industrial area in China (Begum *et al.*, 2009).

4.9 Complexation Ultra-filtration

4.9.1 FT-IR Spectroscopy

The FT-IR spectrum of synthesized CMS is shown in Figure 4.3. The broadband between 3600 and 3000 cm^{-1} is assigned to –OH stretching and is due to hydrogen bonding involving the hydroxyl groups in starch molecules. The band at around $2922cm^{-1}$ is assigned to $–CH_2$ symmetrical stretching vibrations while the band at 1610 and $1393cm^{-1}$ suggests strong absorption peaks for asymmetric and symmetric $-COO^-$ vibrations (Li *et al.*, 2011; Spychaj *et al.*, 2013). This bond confirms the introduction of $–OCH_2COO^-$ group into the starch molecule. The presence of the carboxymethyl groups distributed along the starch chain bestows it with an increased reactivity and solubility in water (Musarurwa & Tavengwa, 2020)

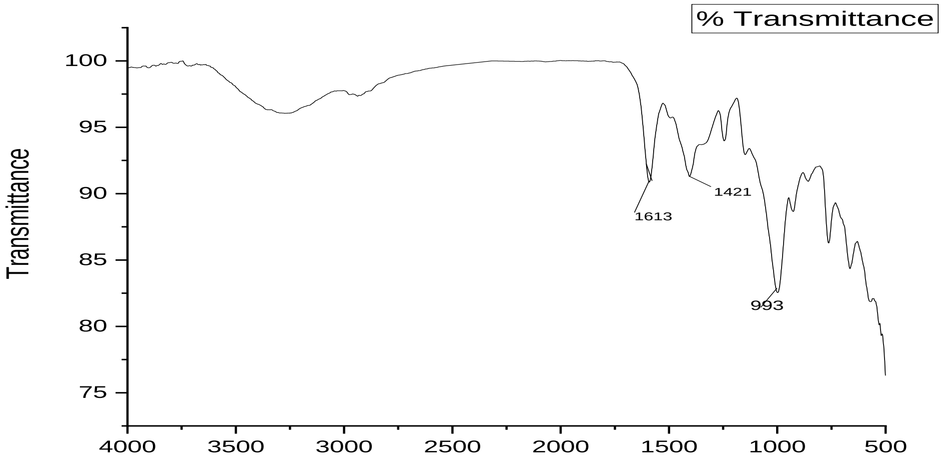

Figure 4.3: FTIR spectra of synthesized carboxymethyl starch

4.9.2 Removal of Heavy Metals

Complexation of heavy metal ions with water-soluble polymers results to formation of high molecular weight species (Bhat *et al.*, 2015). The high molecular weight complexes are large and thus cannot penetrate the ultra-filtration membranes that act as molecular size barrier. This leads to retention of the metallic ions in the filtration unit. Concentration of heavy metals in the initial feed solution and in the permeate solution after ultra-filtration for water samples are presented in Table 4.9. The results revealed that CMS had chelating percentage of 66.19% for Zn, 66.90% for Pb, and 66.18% for Cu while the chelating percentage was lower, 14.37% for Cr. On the other hand, CMS indicated high chelating percentage (92.31%) for Cd. The results displayed that the synthesized carboxymethyl starch has a greater efficiency to complex and retain heavy metal ions hence a potential material for removal of heavy metals from water.

Table 4.9: Concentration of heavy metals in solution before and after addition of Carboxymethyl starch

Heavy metal	Concentration of feed (mg/L)	Concentration of permeate (mg/L)	Chelation of heavy (Percentage, %)
Zn	7.46	2.53	66.19
Pb	28.16	9.32	66.90
Cu	11.38	3.85	66.18
Cr	8.98	7.69	14.37
Cd	1.30	0.10	92.31

Findings from this research are in agreement with previous reports by other scientists who reported caborxymethyl starch as a very viable complexion agent for heavy metals (Wang *et al.*, 2010; Li *et al.*, 2011; Musarurwa & Tavengwa, 2020). Percentage complexation values obtained in this study compare well with 90% heavy metal removal efficiency for metal concentration ranging between 10 to 112 mg/L reported by Gunatilake, 2015. Baharuddin *et al.*, 2019; Lam *et al*., 2017; Mohammed, 2017; also reported modified starch as an efficient medium for removing heavy metals from waste water. However, the percentage chelating effect recorded in this study were slightly lower than those recorded (70.98 – 90%) in a previous study (Baharuddin *et al*., 2014).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.0 Introduction

This chapter gives a summary of conclusions based on the five objectives that this study aimed to achieve and recommendations from findings obtained from the study.

5.1 Conclusions

5.1.1 Sources of Water Pollution in Machakos Municipality

This study revealed that solid waste, untreated sewage and municipal effluents that are released directly into the urban river systems due to broken sewer lines are major primary sources of pollution to water in urban river systems in Machakos municipality.

5.1.2 Physico-chemical Parameters of Water

Temperature, pH and total dissolved solids average values were found to be within WHO recommended limits for surface water. Electrical conductivity mean value on the other hand exceeded WHO acceptable standards for surface water. The high electrical conductivity was an indication of pollution of the water and thus the study concluded that the water from the Iini and Ikiwe urban stream required prior treatment before domestic use.

5.1.3 Heavy Metals in Water, Soil and Vegetables

There was a variation in the levels of heavy metals in the different sampling sites for urban streams water, soil and vegetables. The concentration of heavy metals in the urban streams water and soil were within WHO permissible limits for surface water and agricultural soil thus safe for agricultural use. However, heavy metals have shown a substantial build-up in soils than in the water because of continued use of the water in irrigation.

Cd and Cu were within WHO permissible limits for human consumption in spinach and while Pb, Zn and Cr slightly exceeded WHO permissible limits in spinach. On the other hand, Cd, Cu and Pb were within WHO permissible limits while Zn and Cr exceeded WHO limits on kales. Results from the study indicated that irrigation with contaminated urban stream water containing variable amounts of heavy metals contributed to an increase in the concentration of heavy metals in the soil and the vegetables grown using the polluted water. Furthermore, this study thus concludes that there are possible health risk hazards to the human consumers of spinach and kales from the area of study as they are exposed to unsafe levels of Pb, Zn and Cr.

5.1.4 Correlation between Concentration of Heavy Metals in Water, Soil and Vegetables

The mean transfer factors indicated that wastewater irrigated vegetables were strongly enriched with Cd, Cu, Pb, Zn and Cr from both the wastewater and soil where they are grown more especially Cd and Zn. Positive correlations were observed between the heavy metal concentrations in the water, soil and vegetables. Conclusion can be drawn that the heavy metals could be emanating from common sources. Negative correlations were also recorded implying that some of the metals could be originating from different sources or not associated at all.

5.1.5 Complexation Ultra-filtration

Ultra-filtration of water containing heavy metal ions after addition of carboxymethyl starch as a remediation strategy has demonstrated a potential efficiency to remove Pb, Cu, Zn, Cd and Cr heavy metals from water. This study concludes that the cleaner water at the end of the ultra-filtration process can be suitable for recycling or safe for discharge into water bodies without posing health risks to humans and harming the environment.

5.2 Recommendations and Future Research

5.2.1 Recommendations

1. Due to the accumulation of heavy metals in soil and vegetables, this study recommends it is necessary for Machakos public health department and other relevant bodies to continuously monitor water, soil and vegetable quality.
2. To minimize entry of heavy metals into the food chain, National Environment and Management Authority can take lead in ensuring that municipal, domestic and industrial effluents are not drained into rivers and farmlands without proper treatment.
3. Machakos municipality requires a functional municipal and industrial effluent treatment plant, designed to engineering standards and operating based on best practices in order to accommodate the large quantities of sewage generated in Machakos Municipality.
4. Existing policies regarding sewage water and solid waste management need to be enforced to ensure compliance to set standards.
5. Public health officers should sensitize the public on the harmful health effects of consuming vegetables grown using contaminated water.

6. Carboxymethyl starch can be employed as an efficient chelating agent in the removal of heavy metals from water.

5.2.2 Future Research

The further research on the following is recommended;

1. Further research on other heavy metals not covered in this study to determine their concentration levels in urban stream water, soil and in vegetables.
2. Assessment of concentration levels of heavy metals in other different types of vegetables grown along the urban streams other than kales and spinach.
3. Further research to investigate the efficiency of Carboxymethyl starch in removing heavy metals from water from different urban streams.
4. Further research on effect of concentration of Carboxymethyl starch on the percentage of chelation of heavy metals.
5. Further research on regeneration of carboxymethyl starch after the ultra-filtration process.

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