WATER QUALITY OF ATHI RIVER AND ITS TRIBUTARIES BASED ON SELECTED PHYSICAL-CHEMICAL PARAMETERS, HEAVY METALS AND BACTERIAL LEVELS

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DECLARATION

Declaration by the Student

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DEDICATION

This thesis is dedicated to my parents and siblings for their moral and financial support during my entire academic and research period. Also, to miss Julia Priscilla Ouma for her relentless assistance and guidance throughout the entire research period.

ABSTRACT

Pollution is one of the major challenges facing water resources management in Kenya. This study was carried out to assess and monitor water quality status of the Athi River and its tributaries based on selected basic physical-chemical parameters (electrical conductivity, pH, temperature, TDS, TSS, ammonia, sulphide, nitrate, orthophosphate, BOD and COD), heavy metals (Fe, Cu, Cd, Cr, Pb, Mn and Zn) and bacteria (total coliforms, *E. coli,* salmonella and shigella). This is because of the perceived high pollution in Athi River and its tributaries. One hundred and ninety-two (192) water samples were randomly collected employing grab technique. The parameters were analyzed using standard methods for the examination of water and wastewater. For example, heavy metal analysis was done by digestion of 100 mL of water sample by addition of 5 ml of concentrated nitric acid in a fume chamber. Then the digested samples were analyzed using atomic absorption spectrophotometer (AAS SHIMADZU 7000, Japan). The pH (6.4 to 9.78) was generally within the standards for natural portable water while the temperature varied between 17.1 ^{o}C and 31.8 ^{o}C. The electrical conductivity (EC) ranged from 32 µS/cm to 2005 µS/cm while total dissolved solids (TDS) recorded concentration ranging from 20 mg/L to 1243 mg/L. Total suspended solids (TSS, 4 - 840 mg/L), chemical oxygen demand (COD, 14 - 3360 mg/L and biochemical oxygen demand (BOD, 1 - 640 mg/L)) recorded wide concentration range. Other parameters measured include sulphide (<1 - 192 mg/L), nitrate (ND - 44 mg/L), orthophosphate (0.1 -18 mg/L) and ammonia (ND - 204 mg/L). Levels of analyzed heavy metals were detected in the overall range of ND – 7.6 mg/L with cadmium, copper and chromium not detected. Iron levels ranged from 0.01 – 7.6 mg/L, lead ND – 0.7 mg/L, zinc ND – 3.4 mg/L and manganese ND – 4.3 mg/L. High bacterial counts recorded in collected water samples were: Salmonella ($1 – 1.01\times10^2$) counts, *Escherichia coli* ($4 - 1.79\times10^7$ cfu/100 mL), Shigella ($1 – 1.11\times10^2$ counts) and total coliforms ($20 – 6.03\times10^7$ cfu/100 mL). Some of the physical-chemical parameters (such as, BOD and COD) values in effluent samples discharged into the rivers by the wastewater treatment plants were higher than the KEBS and WHO tolerable levels. Consequently, more effort should be put by the relevant government agencies and departments to address pollution challenges in the Athi River basin.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
ACA	Athi Catchment Area
ADCP	Acoustic Doppler Current Profiler
APHA	American Public Health Association
AWWA	American Water Works Association
BCM	Billion Cubic Metres
BOD	Biological Oxygen demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EC	Electrical Conductivity
FAS	Ferrous Ammonium Sulphate
FC	Faecal Coliform
RVCA	Rift Valley Catchment Area
TCA	Tana Catchment Area
TC	Total Coliform
MCM	Million Cubic Metres
TDS	Total Dissolved Substances
TSS	Total Suspended Substances
UN	United Nations
UNICEF	United Nations International Children’s Fund

USAID	United States Agency for International Development
USEPA	United States Environmental Protection Agency
UV/VIS	Ultra-Violet Visible
WERF	Water Environment Research Federal
W.H.O	World Health Organization
WRA	Water Resources Authority

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CHAPTER ONE

INTRODUCTION

1.1 Background Information

Generally, water is the second most abundant natural resource after air. It covers approximately 326 million cubic miles of the planet, that is, nearly 71% of the total Earth's surface, of which 96.5% is salty ocean waters. Fresh water constitutes 2.5%, of which about 69% is locked up in glaciers and the polar ice caps and 30% ground water. Less than 1% is available as sweet fresh water lakes, rivers and streams (Bureau of Reclamation, 2020; Fraser Cain, 2005).

Though Africa has abundant water resources, it experiences large disparities in water availability between and within regions. For example, about 50% of Africa's total surface water is within the Congo River basin while 75% of total water resources is concentrated in eight major river basins, mainly in the Sub-Sahara. Available freshwater per capita in Africa varies significantly across the African countries. Whereas the Democratic Republic of Congo has highest availability (250,000 m^3 per capita per year), Tanzania (2035 m^3), Uganda (1273 m^3), Burundi (840 m^3) and Kenya (570 m^3) have relatively lower availability (Travails, 2010; Mocha *et al.*, 2010).

Kenya is classified as a water-scarce country with its natural endowment of renewable freshwater currently at 570 m^3 per capita per annum and could reduce to 235 m^3 per capita per annum by 2050 (Ministry of Water and Irrigation, 2008; Mocha *et al.*, 2010). United Nations classifies a country as water-scarce if its renewable freshwater potential is less than 1,000 m^3 per capita per annum. The scarcity is more severe in the Arid and Semi-Arid

Lands (ASALs) which has led to the strain on women and children having the task of searching for water especially for domestic use (Mulwa *et al*., 2021).

Five water towers account for approximately 90% of Kenya's total surface water renewable resources supply annually. Namely: Lake Victoria Basin, Ewaso Ng'iro basin, Tana River basin, Rift Valley Basin, and Athi River basin.

The most productive is Lake Victoria basin, accounting for about 59% of surface water resources and about 54% of the total freshwater resources (that is, approximately 13.80 BCM). The Tana River Basin supplies almost 19% of freshwater renewable resources (that is, approximately 3.70 BCM) and it comprises of Thika River, a key water source for Nairobi River. Tana River is the longest river in Kenya flowing approximately 1,050 kilometers from Mt. Kenya and Aberdare ranges through arid and semi-arid lands (ASALs) before draining into Indian Ocean. The Rift Valley Basin has no outlets since it is an internal basin. It accounts for nearly 14% of Kenya's renewable fresh surface water (that is, approximately 3.26 BCM). Its headwaters are found in Mau Forest Complex, and it comprises of Lake Turkana (the largest permanent desert lake in the world), Magadi, Naivasha and Baringo, with their water ranging from fresh to saline to brackish. Athi River Basin only accounts for more than six percent of Kenya's renewable surface water (that is, approximately 1.31 BCM) and it extends from Nairobi via Athi River, it ultimately drains into Indian Ocean in Mombasa. Ewaso Ng'iro Basin covers about 36% of Kenya but only accounts for two percent of renewable freshwater (that is, approximately 340 MCM) of the country's surface water resources (GIBB Ltd, 2003; Agwata and Abwao, 1998).

With a projected population of about 77 million by 2050, Kenya faces enormous challenges in the management of its limited water resources to ensure sustainable use

(NCPD & UNFPA, 2020; UNFPA, 2021). The water scarcity in the country is further compounded by pollution which poses a significant risk towards the achievement of universal and equitable access to safe and affordable drinking water for all by 2030 (Sustainable Development Goals, SDG, 6.1). This has been driven by rapid urbanization, poor sanitation systems, industrialization, deforestation and poor agricultural practices.

1.2 Statement of the Problem

Water scarcity is a very crucial problem in Kenya where more than 30 percent of the population (majorly in rural set-up) still uses unsafe, surface water for both drinking and domestic applications without proper treatment (Yu *et al*., 2019). This is compounded by pollution which is a major challenge facing its sustainable water consumption. It poses a significant risk towards the achievement of the universal and equitable access to safe and affordable drinking water for all by 2030 (Sustainable Development Goals, SDG, 6.1). It is more severe since water pollution regulatory institutions, legal frameworks and enforcements are weak (WHO/UNICEF, 2021). This has been driven by rapid urbanization, poor sanitation systems, industrialization, deforestation and poor agricultural practices.

Very little is known about the physical-chemical, heavy metal, and bacterial composition of surface water sources from rivers within the Athi River basin area. For a high standard of living and the prevention of disease, adequate quality water must always be accessible. The Athi River basin is home to several human activities, which add to pollution. The majority of the land in this basin is used for farming, such as, production of vegetables, corn, and livestock rearing. Particularly those near rivers within Athi River basin have messy environments, and there is no evidence of riparian protection. Due to bacterial water contamination and sediment runoff from agricultural land into rivers, poses a major concern. Additionally, the Athi River basin's water quality is threatened by the informal settlements and industrial areas where some of these rivers flows through, poorly managed garbage disposal and management, which is a significant source of pollution in the basin.

Many households around the Athi River collect water straight from the rivers for domestic consumption, livestock watering, household-level treatment is insufficient. Drinking untreated water drawn directly from surface water sources would have a negative impact on consumers' health. This is as a result of water pollutants which causes a vast array of health problems such as cancer, endocrine disruption. For instance, cadmium exhibits biological toxicity and it is mutagenic, carcinogenic, and teratogenic. It’s easily absorbed by crops causing harm crops development and growth affecting crop yield and quality (Solgi & Parmah, 2015). It causes damage to the liver, kidneys, reproductive organs, toxicity to immune, lungs, cardiovascular systems and bones in humans and other higher organisms. Lead also as a heavy metal, induces dysfunctions in the reproductive systems, renal and neurologic particularly in young children.

1.3 Objectives

1.3.1 Broad Objective

The main objective of this study was to assess and monitor water quality status of the Athi River and its tributaries based on selected basic physical-chemical, heavy metals and bacteriological parameters.

1.3.2 Specific Objectives

i. To determine selected physical-chemical parameters in river water within the Athi Basin area.

ii. To determine the bacterial contamination level in river water within the Athi Basin area.

iii. To determine the concentration of selected heavy metals (Fe, Cu, Cd, Cr, Pb, Mn and Zn) in river water within Athi Basin Area using atomic absorption spectrophotometer (AAS).

iv. To compare the registered physical-chemical, heavy metals and bacterial levels with the KEBS/EAS/WASREB/WHO guidelines.

1.3.3 Hypothesis

I. HO_1: There was no pollution to determine basing on selected physical-chemical parameters in river water within the Athi Basin area.

II. HO_2: There was no bacterial contamination to determine in river water within the Athi Basin area.

III. HO_3: There was no heavy metals (Fe, Cu, Cd, Cr, Pb, Mn and Zn) pollution to determine in river water within Athi Basin Area using atomic absorption spectrophotometer (AAS).

IV. HO_3: To compare the registered physical-chemical, heavy metals and bacterial levels values in river water within the Athi Basin area with the KEBS/EAS/WASREB/WHO guidelines.

1.4 Justification

Kenya suffers from water scarcity, yet the limited water available is threatened by pollutions. Consequently, access to safe and clean water for the local population is hindered. For example, more than 30 percent of the population, majority of which lives in the rural areas uses unsafe, surface water for both drinking and domestic uses without any treatment. This exposes them to the risks of outbreak of water borne diseases and economic losses. The high cost of water treatment and capital investment needed for water services and infrastructure further compound the challenges. Furthermore, inadequate water quality monitoring plans for effective decision making and water resources management is an impediment to access to safe and clean water.

Due to the rising water demand in Kenya, the government has initiated several projects to boost water supply. For example, it has embarked on the construction of a multipurpose dam in Thwake (Thwake dam) to provide water for domestic, power generation and irrigation in the lower Eastern region. However, the feasibility and sustainability of the project has received a lot of concern from the stakeholders because of the perceived pollution of Athi River which will supply most water into the dam.

From the foregoing, there is need for a comprehensive water quality assessment and monitoring in the Athi River basin to generate data and information that is vital for development of viable strategic pollution control actions in the area. Moreover, such studies would identify pollution hotspots in the area for effective interventions.

1.5 Significance of the study

By evaluating and tracking the water quality state of the Athi River and its tributaries based on chosen fundamental physical-chemical, heavy metals, and bacteriological parameters, this study will help in determining the consequences of pollution. The findings of this study will therefore be useful in locating the origins of water contamination and in bolstering preventative measures against it. Therefore, this study will serve as a baseline for future research on surface water quality monitoring by analysis of physical-chemical parameters, heavy metals and bacteria in Kenya, Africa and globally.

1.6 Scope and limitation

The scope of this study was at Athi River basin, Kenya. The purpose of this research was to assess pollution in the basin based on the analysis of physical-chemical, heavy metals and microorganisms water quality parameters. The selected parameters included biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), pH, electrical conductivity (EC), total dissolved solids (TDS), ammonia, sulphides, orthophosphates and nitrates and selected heavy metal (Fe, Cu, Pb, Mn, Cr, Zn and Cd). Additionally, microorganisms (*E. coli*, total coliforms, shigella and salmonella) indicators were assessed. However, the study was limited in time and scope of pollutants thus their occurrence in the basin cannot be deduced from this study alone.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Water is one of the most important needs for life. Therefore, water pollution has health, environmental and economic ramifications. For example, pollution may lead to change in natural cycles (for instance, nutrient cycle), loss of biodiversity and fish stock, algal blooms, outbreak of water borne diseases, high prevalence of terminal diseases among the many, cancer and food insecurity (USEPA, 2020; Data Stream, 2021; Denchak, 2018; Evans *et al*., 2018; Vallero, 2011, 2019).

As a result, water quality can be described extensively in the scientific literature. The most popular definition of water quality is "it is the physical, chemical and biological characteristics of water". Water quality is therefore the evaluation of the physical, chemical, biological, and radiological properties of water, that is, a measure of the water condition relative to the requirements of one or more biotic species and/or to any human need or purpose (Omer, 2019). Water availability is the quantity of water that may be used for human purposes without adversely hurting ecosystems or other users. It takes into account the needs of ecosystems and people, as well as the fair allocation of water among users and indications of water resource stress. All water resources are related in some way through the hydrologic cycle. Surface water resources from both runoff and groundwater discharges (Farms & Hillsborough, 2013; Xu & Wu, 2017).

Safe drinking-water access is a basic human right and fundamental to development of humans. Lack of access to safe fresh drinking-water sources, coupled with inadequate hygiene and sanitation, still remains the most critical challenge to public health worldwide. Safe and clean drinking-water is essential commodity for sustaining life. It is the basis for growth, human health, development and survival hence, a basic human right. It's recognition as basic human right contributes to the disease prevention and human beings survival, because it is not only used for drinking, but also many other purposes such as, food production, hygiene, agriculture, industry and cooking (WHO, 2007).

Drinking contaminated unsafe water impairs health via diseases such as cholera, diarrhoea, dysentery, typhoid, polio and can eventually cause death. For example, it is estimated that over 400,000 diarrhoeal deaths globally are caused by contaminated drinking water each year. Untreated excreta contaminate surface water and groundwater used for irrigation, drinking-water, household purposes and bathing. Contamination of water with chemicals continue to pose health burdens, whether natural in origin for example, arsenic and fluoride, or anthropogenic such as, nitrate (Water, Sanitation and Hygiene, 2015; Assembly, 2019; Guidelines, 2020).

According to WHO (2019), one in every three people globally don't have access to clean and safe drinking water. Also 1 in 10 people (785 million) lacks basic drinking water services, this includes about 144 million people who still depends on surface water sources. On the other hand, about two billion people use a drinking water source contaminated with faeces and other related water contaminants. By the year 2025, half of the world's population will be living in water-stressed areas. These areas include Middle East, Africa, and parts of Asia.

For this investigation, the Athi River was chosen (**Figure 3.1**). Geographically, it is located between Latitudes 1 ° to 4.5 ° South and Longitudes 37 ° to 40 ° East, and it has an estimated area of 58,639Km^2. The Athi River, Kenya's second-longest river (about 390 km), and its tributaries are primarily responsible for draining the basin. The counties of Nairobi, Makueni, Taita Taveta, Kwale, and Mombasa are all included in the basin, together with portions of Kiambu, Machakos, Kajiado, Kilifi, Kitui, and Nyandarua. Before emptying into the Indian Ocean, the river travels through the towns of Kiambu, Nairobi, Kajiado, Machakos, Malindi, Kilifi, and Mombasa.

The upper reaches of the basin are highly urbanized with regular rainfall while the middle and lower reaches are generally arid and semi-arid with low population density. The Kikuyu springs and Ondiri Swamp-upstream of Athi River form critical groundwater recharge points in the area. On average, the basin receives an annual rainfall of 739 mm and a low groundwater recharge rate of 296 million cubic metres per year (Nyingi *et al*., 2013).

Athi River, which empties into the Indian Ocean, has 1,656 mcm of water available annually. The upper catchment above the Thwake confluence accounts for around 60% of its natural flow. Between the confluence of the Thwake and Kiboko, an additional 20% of the total runoff is produced. Simulated total annual natural surface water flow from all rivers in the Athi Basin is equal to around 2,555 mcm (Aurecon AMEI limited, 2020).

Of the six basins in Kenya, the Athi Basin has the largest urban water demand. Future population growth and urbanization are predicted to cause a major rise in the basin's water consumption. This is because the river passes through two major cities in the country (that is, Nairobi and Mombasa cities) with other upcoming towns and cities. These cities have high water demand due to several land-use changes in regard to agricultural productivity, urbanization (due to upcoming cities such as, Machakos, Konza, Tatu and Diani cities), and industrialization and population settlement density. These factors have adverse effects on the water resources and subsequently on the environment, mainly water quality in general (Kithiia, 2007).

Rainfall patterns, topography and human settlement-cum-activities highly influence land use patterns within the study area. For example, agriculture dominates the economy of the upper catchment area (Kiambu and kikuyu towns) providing a livelihood to about 70% of the population. Moving towards the city and the southern parts, this changes significantly. Industrial activities dominate within the city, while livestock keeping and small-scale irrigation are more pronounced in the southern parts (Aurecon AMEI limited, 2020; Kithiia, 2007).

Due to erosion and other human activity (such as agricultural operations) in its upstream portions, the river contains a massive quantity of suspended sediments. It is estimated that the river discharges 2,057, 487 tons of silt into the Indian Ocean per year. The Nairobi River drainage basin is the most intensively and extensively affected sub-basin by human activities such as human settlement, agricultural activities mainly small-scale vegetable growing (for instance, Nairobi River at Juja farm, Thiririka at kikuyu and Ruiru rivers) and industrial activities. Other land use activities include flower gardening, tree nurseries and small-scale farming along most of the river banks in this sub-drainage basin.

Physical-chemical water quality indicators are based on various values of physical-chemical qualities in water samples. They are vital in monitoring water quality (APHA, 2017; Brandi & Wilson-Wilde, 2013). A number of tools and scientific procedures have been developed for water quality assessment (Dissmeyer, 2000). The procedures include analysis of different water quality parameters such as electrical conductivity, pH, temperature, biological oxygen demand, dissolved solids, chemical oxygen demand, nitrates, orthophosphates, sulphides, suspended solids amongst many other parameters (Atiku *et al*., 2018). According to Addendum & Third,(2008); Gazi *et al*., (2012); Herschy, (2012) and WHO, 2011a) high concentration levels of physical-chemical parameters above WHO threshold limits and other regulatory bodies can affect the quality for drinking water.

Effective monitoring of physical-chemical, heavy metals and microbiological parameters can help identify pollution, pollution sources and hence aid in controlling pollution in water (Chandra *et al*., 2006). This is a special initiative with significance of protecting human health from water contamination (APHA, 2017). Coliform group of bacteria are principal indicators of water suitability for domestic or other uses. Experiments have established the significance of density of coliforms particularly, that of thermotolerant coliforms or *E. coli* (previously known as faecal coliforms) as a criteria for water quality, and the groups characteristics and cultural reactions have been studied extensively (Atiku *et al*., 2018; Brandi & Wilson-Wilde, 2013)

Indicator microorganisms, such as, coliforms (that is, total coliform (TC) and faecal coliforms (FC)) are useful for the faecal pollution assessment (APHA, 2017). Knowledge of detailed faecal pollution in aquatic ecosystem is very crucial in maintaining healthy water resources for both economic and recreational purposes (Farnleitner *et al*., 2001). High concentrations levels of vibrio cholerae and heterotrophic bacteria is of great threat together with elevated water temperatures which increase organic matter decomposition.

The high concentrations of vibrio cholerae bacteria cause cholera through faster pathogenic growth rate in aquatic ecosystems (Koelle *et al*., 2005).

Environmental pollution with metals, semimetals, metalloids and microorganic contaminants is a serious problem globally and requires more attention. Heavy metals contamination shows unfavourable consequences for both flora and fauna. This causes water toxicity through leaching into the water sources, resulting in decreased performance and product quality in agriculture. This negatively impacts both living organisms as well as the entire public.

2.2 Water Pollution

Generally, water pollution is the contamination of water resources by substances which impair its ability to provide ecosystem services. Pollutants get into the water bodies through natural processes and anthropogenic activities. Natural processes such as weathering of the bedrock minerals and atmospheric processes (for instance, atmospheric deposition) may change the natural composition of water resources. In the natural environment water may contain suspended solids as well as dissolved solids (Khatri & Tyagi, 2015). On the other hand, human activities introduce diverse kinds of pollutants into the water resources. Such activities include agricultural, industrial processes, commercial enterprises and domestic activities (Kithiia, 2007).

Overall, pollution can be attributed to point and non-point sources. Point source pollution originates from a single and identifiable source such as industrial discharge, wastewater treatment facility effluent and landfills. They are relatively easy to trace and identify (Shahabudin & Musa, 2018). On the other hand, non-point pollution sources are diffuse in nature and relatively difficult to identify such as runoff from farmlands (Liu *et al*., 2015).

Generally, pollution can be categorized into four broad groups based on the nature of contaminants. These include physical, chemical, biological and thermal.

2.3 Pollution Types and pollution sources

Here in case of this study water pollution is categorized into four groups, that is, physical, thermal, chemical and biological pollution. Whereas physical water pollution primarily impacts physical properties of water (for instance, turbidity), chemical pollution comprises both organic and inorganic chemical substances which impair chemical water quality. On the other hand, biological pollution involves contamination of water by mainly microorganisms such as bacteria. (Data Stream, 2021; Denchak, 2018; Evans *et al*., 2018; USEPA, 2020; Vallero, 2011, 2019).

2.2.1 Thermal pollution

Thermal pollution refers to the excessive lowering or raising of temperature in water below or above normal seasonal ranges in water bodies. This is as result of discharge of cold or hot effluents into water resources. Significant change in temperature may affect ecosystem functioning, precipitate loss of biodiversity, change of natural cycles (for instance, nutrient cycle) and influence intensity of algal blooms and disease outbreaks (Vallero, 2011, 2019).

Heat generally initiates cumulative environmental impacts, for instance, heat exchange and receiving water bodies changing conditions. Some chemical reactions depend majorly on temperature. For example, toxic chemical species to organisms are bioavailable and more soluble with increase in temperature. This increases exposure of organisms in water to harmful substances. Temperatures elevation increases concentration of toxic metals such as mercury. Low concentrations of dissolved oxygen create a reduced environment where heavy metals and their respective compounds could form sulphides and other toxic compounds to fish and other aquatic organisms. Therefore, these effects can further be increased by the synergistic impact of the combination of the hypoxic water and minimized heavy metal and their compounds that harms water resources ecosystems (Inspire, 2021; Shears & Ross, 2010; Vallero, 2011, 2019).

Water temperature bodies increases a result of human activities which may include clearing vegetation from stream banks. This results in removal of streams natural shading; runoff through uncovered land leads to warm or hot water from surfaces of heated land. Also, disposed heated effluents from industries (for instance, thermal discharges from steam-electric power plants). On the other hand, water sources temperature decreases as a result of cooler water inflow from dams or of industries cooling systems (Kennedy, 2004).

2.2.2 Physical pollution

Physical water pollution primarily impacts physical properties or appearance of water such as turbidity, colour and suspended solids. Sediment or suspended organic materials in streams, lakes and rivers water from soil erosion are examples of physical contaminants. Consequently physical pollution affects light penetration, oxygen circulation and hampers survival of aquatic animals such as fish (Data Stream, 2021; Denchak, 2018; Javeed, 2020; Suner, 2019).

Major sources of surface water contamination are both natural and anthropogenic. Natural is caused by runoff which carries sediments from construction and agricultural lands soil erosion into the water sources. On the other hand, anthropogenic is either accidental or deliberate water pollution by man discarding waste (for instance, plastics) into the water bodies.

2.2.3 Chemical pollution

Chemical pollution refers to the contamination of water bodies by organic and inorganic chemical substances. Such chemicals include toxic metals, radioactive compounds, agrochemicals and industrial chemicals. These chemicals have both human toxicological effects, thus deleterious to humans and ecosystems. For example, some pesticides are carcinogenic and may cause cancer when taken through drinking water.Also, heavy metals such as arsenic as a carcinogen causes skin, liver, bladder and lung cancer (Hadzi *et al*., 2015).

I. Inorganic contaminants

These are class of contaminants discharged by chemical based and allied industries such as pharmaceuticals, refineries and fertilizers industries. These contaminants comprise mostly of toxic heavy metals, different nutrients types (for instance, nitrites, phosphates) and salts (for instance, chlorides, sulpates, carbonates) that mostly occur in the form of dissolved anions and cations. Inorganic contaminants presence in water can be measured by their chemical parameters (for instance, hardness, which is caused by magnesium or calcium components).

Inorganic contaminants can also be measured by heavy metals presence in water. The term ‘heavy metal’ precisely means metals with density greater or higher than that of water, or on the other hand they are metals having atomic number greater than 20 (Tchounwou *et al*., 2012). Heavy metal solubility increases with a fall in water pH levels therefore their particles become more mobile. This makes metals ions more concentrated hence high toxicity in soft waters. The heavy metals might become ‘locked up’ in sediments in the river bed, where they can be retained for many or several years. Streams and tributaries coming from draining mining areas are often very acidic due to the effect of acids from the mine companies and contain high concentrations of dissolved metals with little aquatic life.

Heavy metals pollutants sources in the surface water environment are both natural and anthropogenic. The geological or natural heavy metal sources in the water ecosystem include volcanic eruptions and weathering of metal-bearing rocks. Global industrialization trends, for example, mining, processing, agricultural activities via pesticides and urbanization on Earth are causes of increased anthropogenic sources of heavy metals in an aquatic environment (Ali *et al*., 2019).

II. Organic contaminants

These are carbon-based chemicals (for instance, gas/liquid phase volatile compounds, organic solvents, timber, petroleum-based wastes and pesticides). Contamination through organic materials just as inorganic contaminants can cause serious health impacts like nervous system disorder, hormonal disruptions, and cancers in humans and higher organisms. Most toxic organic compounds are not biodegradable, or degrades slowly, therefore they persist in the environment. Others are magnified in the food web, while some can cause cancer in humans. On the other hand, some can be converted into carcinogens when they react with chlorine used for water disinfection (for instance, Trihalomethanes (THMs)). Some affects or even kills fish and other aquatic organisms, with some being a nuisances, giving water and fish an unpleasant smell or offensive taste (Sasakova *et al*., 2018). Pesticides Industrial and domestic wastes are the major anthropogenic organic contamination sources.

III. Radiological contaminants

These are pollutants caused by radioactive elements. They are hazardous because of their radioactive decay produces ionizing radiations (namely, alpha, α, beta, β, gamma, Γ, rays and free neutrons). Their contaminant concentration determines their hazardous degree, radiation energy they emit, radiation type and proximity of the contamination of the body. Radioactive material sources could be soils or rocks on which the water flows through and/or some industrial wastes. Erosion of natural deposits of radioactive minerals emits radiations (for instance, alpha, α, beta, β). Radiological elements (like. Ra^{226}, Rn^{228}, U^{226} and Ra^{228}) tends to be a nuisance in groundwater rather than in surface water (Sharma & Bhattacharya, 2017).

2.2.4 Biological contamination

These are pollutants caused by the presence of microorganisms (for instance, bacteria, algae, viruses or protozoan). Algae are in generally microscopic, single celled and are quite abundant. They are nutrients dependent especially phosphorus in water ecosystem. Excessive algal growth does not only impact water taste and odour; it also produces unwanted slime growths on the carriers and clogs filters (Sharma & Bhattacharya, 2017).

In addition to their environmental effects, many of their characteristics can directly affects human health, through drinking water and recreational activities (for instance, health effects in swimmers is due to harmful algal blooms, pathogens, shellfish and consumption of affected fish), or indirectly through diminishing of the food supply as a result of reduction in fish and other food source in aquatic habitat through depletion of their population due to death or migration to other favorable aquatic habitat (USEPA, 2020).

These organisms are responsible for diseases transmitted through water, such as dysentery, typhoid fever, hepatitis, cholera, schistosomiasis and polio (Postigo *et al*., 2017).

Salmonella's principal habitat is the intestinal tract of warm-blooded animals for instance, humans while Shigella is human specific. Constantly these microorganisms are highly found in environmental samples, since they are excreted by humans, wild life animals, pets and farm animals in general. They have been repeatedly detected in various types of natural aquatic systems such as estuaries, contaminated ground water, rivers, coastal waters as well as lakes. Fecal contamination from the indirect household sewage discharge, agriculture pollution, municipal sewage, storm water runoff and infected people are the direct sources of these pathogens in natural waters (Chouhan, 2015).

2.3 Effects of pollution

Surface runoff of silt, sand and clay from agricultural land into waterways is a natural water pollution process. It builds up as sediments in the floodplains and wetlands. Logging, ploughing, and buildings or road construction or land disturbances causes excessive sediment runoff. These sediments become water pollutants if they muddy a water resource and hence hinders photosynthesis, clog the feeding apparatus or gills of animals and bury aquatic ecosystems. These sediments may also have toxic chemicals attached to them, which can alter the chemical properties of the water.

Water resources having low pH supports a lower variety and quantity of life. For example, at a pH of 7.0 – 9.2 most marine plants grow best. For instance, population of plants declines as pH decreases, decreasing aquatic birds' nourishment. Continued decrease in pH, decreases the population of freshwater organisms (for instance, crayfish, shrimp, some fish and clams). At a pH of 5.5, leaf litter and other wreckages decomposing bacteria starts to perish, cutting off plankton nutrient sources. Great quantities of aluminum in a lake brought by acid runoff, causes excess stress to fish populations, leading to smaller size and lower body weight. Alien fish species overcomes native fish for food and habitat.

Nutrients enter water resources from runoff from agricultural land, atmospheric and organic matter recycling within the aquatic environment. Depending on prevailing environmental conditions (for instance, pH and temperature) ammonia can be poisonous to fish and other aquatic creatures. Excessive nutrients concentration comes majorly into water resources from animal and human wastes, fertilizers and detergents. Runoff, raw Sewage, drainage from wastewater treatment plants, domestic and industrial effluents entering water resources directly, from either a deliberate act or from spills and leaks from wastewater lagoons, can carry an enormous quantity of nutrient which might be lethal for fish survival (Javeed, 2020).

Eutrophication is part of water resources natural aging process progressing from oligotrophic level to mesotrophic level to eutrophic level. Excess nutrients presence drastically reduces natural aging pace from thousands to just a few years. Excess of these nutrients act as fertilizer for algae and other aquatic plants during eutrophication leading to bloom. Death of aquatic plants and animals, expands bacteria populations to consume their tissues. These bacteria deplete oxygen from water since the they aerobically consume the dead organic matter. Gases such as oxygen bubbles out into the atmosphere because of the warming effects of decaying tissue in water resources thus rendering the water hypoxic; hence, most aquatic animals for instance, fish cannot survive in it. Therefore, becoming a lifeless or dead zones, regions that are most unreceptive to life. Different species starts to appear as native ones leave or die (Javeed, 2020)

Due to the toxicity nature and other adverse effects of heavy metals. Water pollution by heavy metals has been of great concern. Introduction of these heavy metals into water sources creates a greater risk for the general population that depends on them for both drinking and domestic water consumption. For example, amongst toxic heavy metals, cadmium causes hypertension, renal dysfunction, lung inefficiency, bone degeneration and liver damage in humans. International Agency for Research on Cancer (IARC) has designated cadmium as category I carcinogen (Módenes *et al*., 2009).

A variety of ailments in humans can be caused by heavy metals depending on exposure degree. They can vary from severe circulatory system damages of the nervous system, kidney and liver damages to minor skin irritations. For example, selenium (Se) is required in trace amounts, but overexposure to selenium causes accumulation in tissues. This leads to health problems such as fatigue, loss of fingernails and hair, irritability and kidney damage on chronic exposure, liver tissues, nervous system and circulatory (Nongbri & Syiem, 2012; Sunda, 1988).

Similarly, zinc (Zn) is also essential requirement for good health, excessive exposure to zinc is also harmful. Its toxicity can occur in both chronic and acute forms. With acute effects of excess zinc intake includes appetite loss, nausea, abdominal cramps, vomiting, headaches and diarrhoea. Chronic zinc effects include reduced levels of high-density lipoproteins, altered iron function, copper deficiency and reduced immune response. Drinking of contaminated water with Manganese (Mn) is associated with behavioural and neurological effects. There is an association between liver disease and manganese accumulation. Acute exposure to nickel (Ni) has been associated with a variety of clinical signs and symptoms which includes giddiness, headaches, coughing, gastrointestinal disturbances, wheezing and visual defects (temporary left homonymous hemianopia). Long-term cadmium (Cd) exposure causes and bone defects (osteoporosis, osteomalacia), obstructive lung disease and cancer and renal dysfunction in humans. Despite copper (Cu) being an essential element but high doses cause kidney and liver damage, intestinal and stomach irritations and anaemia. High dose lead (Pb) exposure in humans manifests as toxic biochemical effects causing problems in the haemoglobin synthesis, joints and reproductive system affect, kidneys, nervous system and gastrointestinal tract (Jacobs *et al*., 2014; Järup, 2003).

Therefore in regards to the above information, water pollution effects can be categorised into four different categories, that is, ecological, economic, social and health.

2.3.1 Ecological effects

Water pollution destroys biodiversity by depleting aquatic ecosystems and triggering unbridled phytoplankton proliferation in lakes (eutrophication). High concentrations of nutrients especially nitrogen and phosphorus in water resources may lead to algal bloom. Consequently, this reduces the level of dissolved oxygen levels in the water and light penetration leading to death of aquatic animals and plants. In certain cases, harmful algal bloom can produce neurotoxins that affect wildlife from whale to sea turtles (Denchak, 2018). These effects of eutrophication nutrients are a common challenge in surface water globally (Bhagowati & Ahamad, 2019; Glibert, 2017; Ulloa *et al*., 2017).

Water resources ecosystems are also threatened by solid debris, which can strangle, suffocate, and starve animals. Much of these solid debris, such as plastic bags and soda cans, get swept into sewers and storm drains and eventually out to our water resources, turning them into trash soup and sometimes consolidating to form floating garbage patch.

This may obstruct light penetration into the water thereby hampering phytoplankton photosynthesis, hence reduced phytoplankton density, growth rates, and productivity. Reduction of phytoplankton productivity significantly affect fish stock due to limited source of food (Katano *et al*., 2021).

Also, other than human health impacts, water contamination puts resources, for instance, fisheries at risk. Down-stream fish and vegetable crops in most cases, becomes heavily contaminated with water contaminants, for example, contamination with heavy metals and contaminants of emerging concerns (CEC's).

In a toxic algal bloom, algae and algae like bacteria releases harmful toxins with adverse effects to water ecosystem and human health. For instance, shellfish contamination, fish and aquatic bird mortality (Van Deventer *et al*., 2012; Driggers *et al*., 2016; Ulloa *et al*., 2017). Brevotoxins exposure causes respiratory, neurotoxic shellfish poisoning and gastrointestinal illnesses (Hoagland *et al*., 2014; Reich *et al*., 2015).

2.3.2 Economic effect

Deteriorating water quality stalls exacerbate poverty, worsen health conditions, economic growth and reduce food production. For instance, algal blooms and nitrates in drinking water sources drastically can increase treatment costs of water for the removal of contaminants in water. Harmful algal blooms that kill fish severely hurt shellfish and fishing industries, hence reducing fishing income and contaminate shell fish. The tourism industry loses income due to reduction in tourists visiting our country annually, through losses mostly in boating and fishing activities, this is as a result of water bodies being affected by pollution of harmful algal blooms and nutrients (UNESCO, 2015; USEPA, 2013a).

Consumption of unsafe and untreated water infested by waterborne diseases (such as, diarrhoea, dysentery, typhoid or cholera) causing pathogens by a county's population. They are usually confronted with huge and seldom financial burden resulting from financial losses. Mostly from hefty medical bills for treatment, medication, transportation costs, special food diet which can lead to loss of manpower in various sectors. This lowers economic productivity of a nation. Many families may also loose properties for instance,., sell of land and household goods to pay for treatment (Pathak, 2015).

Nutrients rich in water serves as diseases and toxins reservoir. Therefore, they can develop toxic blue-green algae which can poison livestock by causing liver damage, muscle tremors and eventually death. This leads to livestock loss which is a source of income to most farmers.

2.3.3 Social effect

Water pollution renders our water resources unfit for swimming, fishing, and drinking. This impacts recreational businesses and many other sectors that depend on clean water. Also due to deposit of sediments in the bedrock, navigation is hindered therefore tourism and transport are impacted negatively.

2.3.4 Health effect

Due to pollution, there are many health problems associated with consuming untreated water (for example, lungs damage, kidney, reproductive organs, liver and bones, causing toxic effects to the cardiovascular and immune system in humans and other higher organisms) and is associated with various diseases such as cancer.

Drinking or swimming in nutrients polluted waters can cause respiratory, liver, stomach, rashes and neurological effects. For example, nitrates as nutrients contaminate natural portable water in agricultural areas. Storm runoff water can carry these nutrients into clean fresh water resources such as rivers, reservoirs, lakes and dams. The nutrients can lead to algal blooming in the fresh water resources. In water treatment by use of disinfectants such as chlorine can lead to formation of dioxins when the disinfectant reacts with toxic algae. These dioxins can cause damage to the immune system, developmental and reproductive risks, hormonal interference and cancer.

2.4 Indicators of pollution

Several physical-chemical (such as, turbidity, pH, electrical conductivity, chemical oxygen demand (cod), biochemical oxygen demand (bod), dissolved oxygen (do), nutrients, heavy metals and pesticides) and bacteriological (for example, total coliforms and *E. coli*) parameters have been used as water quality indicators globally (Gorde & Jadhav, 2013; Kanase *et al*., 2016; Renu, 2020). These parameters are important in the assessment of the quality of water resources and the possible pollution risks that the resources maybe be exposed to (Alam *et al*., 2007;Bekele *et al*., 2018; Braga *et al*., 2022; García-Ávila *et al*., 2022). Therefore, monitoring of water quality is an essential tool in identifying water pollution problems and formulating measures to aid in minimizing deterioration of water quality (Adesakin *et al*., 2020).

2.4.1 Physical indicators

2.4.1.1 Temperature

Due to its impact on water chemistry, temperature is a crucial component of the physical-chemical parameter analysis. In general, greater temperatures speed up chemical processes.

Higher temperature water, especially groundwater, has the ability to dissolve more minerals from the rock it is surrounded by. As a result, it will be more electrically conductible and have dissolved minerals or particles (U.S. Geological Survey, 2019;Alam *et al*., 2007;Bekele *et al*., 2018;Braga *et al*., 2022;García-Ávila *et al*.,2022).

2.4.1.2 Electrical conductivity (EC)

On the other hand, conductivity measures how well water can carry electrical current. The quantity of ions present in the water has a direct impact on this capacity. The water's conductivity increases with the concentration of these electrolytes in it. Similarly, the less electrolytes there are in the water, the less conductive it is (Alam *et al*., 2007; Bekele *et al*., 2018; Braga *et al*., 2022; García-Ávila *et al*., 2022).

2.4.1.3 Total dissolved solids (TDS)

The total amount of organic and inorganic compounds that are dissolved in water is known as total dissolved substances. They are the little amounts of organic matter and the inorganic substances (minerals and salts) that are in solution in water. These minerals can come from a variety of sources, including both human and natural processes. Because their water travels through a location with high salt content rocks, mineral springs have water with high concentrations of all dissolved components.

2.4.2 Chemical indicators

2.4.2.1 pH

The alkalinity/basicity or acidity of a water source is determined by the pH value of the water. It is a measurement of the activity of hydrogen ions in water. It is also possible to think of it as an abbreviation for potential of hydrogen, which is a way to estimate the amount of hydrogen ions (H^+) in water. According to chemists, pH is determined by the equation: pH is defined as the negative logarithm of the hydrogen ion $[H^+]$ concentration (mol/L) in an aqueous solution (Safe Drinking Water Foundation, 2017).

$$pH = -\text{Log } 10[H^+]$$

2.4.2.2 Chemical and Biochemical Oxygen Demand (BOD and COD)

The amount of oxygen consumed by microbes to break down waste is measured by a process called biochemical oxygen demand (BOD). For example, Dulo (2008) measured BOD of up to 540 mg/L in Nairobi River a tributary of Athi River, which is one order magnitude higher than the maximum allowable limit for effluent discharged into the environment. In the same river, Mbui *et al*, (2016) recorded COD and electrical conductivity of up to 730 mg/L and 600 µS/cm, respectively. However, the available studies are mostly limited to a few small tributaries of the Athi River. The Ngong and Nairobi Rivers have also been measured to have high BOD levels (USAID, 2020). This indicates that rivers have been significantly contaminated by organic waste. The quantity of bacteria requiring oxygen to break down organic waste increases as more organic waste is present, resulting in a high BOD level.

There is a chance that the oxygen will drop to dangerously low levels for aquatic life. The oxygen levels will gradually rise downstream when the river re-aerates as a result of air mixing and algae photosynthesis, which adds oxygen to the water. The loss of oxygen over the course of a 5-day test is used to calculate BOD. Contrarily, COD is a measure of the total amount of oxygen needed to convert all organic material into carbon dioxide and water and does not distinguish between biologically accessible and inert organic matter (Steven, 2017).

2.4.2.3 Heavy metals

Although lead, copper, and even mercury have been used since Roman imperial times, the quantity of heavy metals in the water environment has dramatically grown since the Industrial Revolution. Many of these heavy metals harm children's neural systems and impair their ability to learn. Autoimmune responses can be brought on by exposure to metals like lead and nickel (Steven, 2017). Therefore, the issue of heavy metals water contamination has gained substantial public and scientific attention. Their toxicity to humans and other biological systems, even at extremely low quantities, makes this very obvious (Solana *et al*., 2020). When heavy metals are released into aquatic environments, they can end up in the water and sediment phases as well as potentially bioaccumulate in the biota. Since metals are not biodegradable, both localized and distributed metal pollution causes several serious environmental harms. Metals, unlike other organic pesticides, do not degrade in the environment into less dangerous substances. It has been determined that heavy metals and their compounds are hazardous, and the majority are susceptible to biomagnification.

Since many fish species that are consumed by humans eat invertebrates as food, the build-up of harmful metals in invertebrates is a serious problem. Many estuaries are crucial for conservation, particularly since they are home to large populations of birds that eat invertebrates (Wright & Mason, 1999). Three heavy metals, copper (Cu), cobalt (Co), and zinc (Zn), are fundamentally necessary for the normal growth and function of living things. However, excessive amounts of other metals, such as cadmium (Cd), chromium (Cr), manganese (Mn), and lead (Pb), are thought to be highly toxic for both humans and aquatic life (Muhammad *et al*., 2011). According to Liu *et al*., (2013) when Cr, Cu, and Zn surpass their acceptable threshold values, non-carcinogenic hazards such brain involvement, headaches, and liver illness might result.

For instance, a study conducted on the Jamshedpur Urban Agglomeration in India revealed that the concentrations of heavy metals in the sediments reached 8.1 mg/kg for Cd (background value 0.3 mg/kg) and 135.9 mg/kg for Pb (background value 20.0 mg/kg), and the concentrations of the metals in the fish reached 0.8 mg/kg for Cd and 10.2 mg/kg for Pb (De Voogt, 2015; Kumari *et al*., 2018). As a result, the presence of these heavy metals in aquatic sediments may have long-lasting harmful impacts on biological systems. Through the food chain, they may spread to other creatures even at low quantities. Through the food chain, they endanger human health, hence urgent investigation is needed (De Voogt, 2015).

2.4.3 Nutrients

2.4.3.1 Ammonia

Ammonia (NH_3) interacts with water to create hydroxyl (OH^-) and ammonium ions (NH_4^+). Some free NH_3 is left behind when the pH is higher than 7.2, and this amount grows as the pH rises. These chemical species' equilibrium can be stated by the equation 1.

$$NH_{3\,(g)} + H_2O_{(l)} \leftrightarrow NH_4OH_{(l)} \leftrightarrow NH_4{}^{+}{}_{(aq)} + OH^{-}{}_{(aq)} \text{ -------------------- (equation 1)}$$

Water with high ammonia content makes it difficult for aquatic species to expel NH_3 effectively, which can cause harmful build-up in their internal and blood tissues and even death. The underlying environmental conditions, such as pH and temperature, have an impact on its toxicity to aquatic creatures (Huff, 2013; USEPA, 2013a, 2013b).

2.4.3.2 Nitrates

Nitrates in water can be formed from the oxidation of ammonium (equation 2) and nitrite (equation 3).

$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 2H_2O + 4H^+$, -------------------- (equation 2)

$2NO_2^- + O_2 \rightarrow 2NO_3^-$ --------------------------------------- (equation 3)

The two processes are a natural element of the nitrogen cycle. The nitrate ion (NO_3) is in a stable oxidative state where nitrogen and oxygen have been united. Although it is chemically inert, microbial processes can nevertheless degrade it. Nitrite ion (NO_2^-) includes nitrogen in an unstable oxidation state, making it more reactive than nitrate ion (NO_3^-) (Eisenbrand, 1980; WHO, 2011b).

Nitrification and denitrification can occur in surface water, depending on the pH and the temperature. However, most of the nitrate decrease in surface water is due to plant nitrate absorption. In addition to being created in the air by lightning, nitric acid and inorganic aerosols, as well as nitrate radicals and organic gases or aerosols, nitrogen compounds are also released into the atmosphere by industrial operations, motor vehicles, and intense agricultural activities. These are eliminated via deposition into the earth's surface and surface water resources, both wet and dry (Eisenbrand G., 1980; WHO, 2011b).

2.4.3.3 Orthophosphates

Orthophosphate, which is produced by natural processes, is a form of phosphorus. It is mostly a result of human-impacted sources, such as partially and untreated sewage. Water utilities often use it as a corrosion inhibitor to prevent lead pipes from leaching. Orthophosphates are present in water resources due to runoff from agricultural locations and the use of certain lawn fertilizers. Orthophosphate is commonly present in extremely low quantities in unpolluted streams and is easily accessible to the biological population. Contrarily, polyphosphates are utilized in detergents and for the treatment of boiler water. They are converted to orthophosphate in water, which is easily absorbed by plants (Know your water, 2020).

2.4.3.4 Sulphides

Groundwater and sediment frequently contain sulfide. Naturally, it is created when bacteria with sulfur bases break down organic materials and reduce sulfate (cyanobacteria). It can occasionally be discovered in municipal or industrial effluent (APHA, 2017). Sulfate ions are produced when pyrite, a rock that contains sulphides, dissolves in the interstratified minerals and percolates into groundwater (Adesakin *et al.*, 2020). On the other hand, sulphides can be found in surface water sources as hydrogen sulfide and soluble in water sulphides of alkali and alkaline earth metals. The hydrogen sulphide ion (HS^-) or hydrogen sulfide gas is created when soluble sulfide salts breakdown into sulfide ions and combine with the hydrogen ions in water (H_2S). Sulfide-containing wastewater releases hydrogen sulfide into the air, generating unpleasant odours. Hydrogen sulfide gas (H_2S) in pure water has odour threshold values between 0.025 and 0.25 mg/L. Gaseous hydrogen sulfide (H_2S) is very hazardous and has been responsible for many fatalities.

As a result of its harmful effects on the human olfactory system, hydrogen sulfide (H_2S) might appear to be absent when it is actually present. Acid-volatile sulfide (AVS) reagents at elevated temperatures can partially digest some minerals, for example, iron pyrite, this can result int a significant over estimation of Acid-volatile sulfide (AVS) (APHA, 2017; Brandi & Wilson-Wilde, 2013).

2.4.4 Biological indicators

The biological features of water have a critical role in the management of illnesses brought on by pathogenic organisms. Viruses, bacteria, fungus, algae, and protozoans are among the microorganisms that may be found in surface water and wastewater (Hassan & Hanif, 2014). Several studies have showed that consumption of water contaminated with coliforms, *E. coli*, and Salmonella species results to waterborne diseases such as diarrhoea, arthritis and even death. One of the leading causes of morbidity and death in children under the age of 5 years in the developing countries is diarrhoeal illness (Momtaz *et al*., 2013; Sila, 2019; WHO, 2015). Monitoring the bacteria counts that serve as markers of fecal contamination has historically been used to determine the microbiological safety of drinking water (Sasakova *et al*., 2018). For example, for salmonella and shigella screening of water samples from each sampling source are enriched with selenite 'f' broth and incubated at 37 °C for 18–24 hours.

After gently streaking a loopful of the broth onto a Petri plate containing salmonella-shigella agar (SSA), the dish is incubated at 37 °C for 18 to 24 hours. Transferring the suspicious colonies onto triple sugar iron (TSI) agar allows for the detection of salmonella and shigella (Sila, 2019).

2.5 Pollution control interventions

Controlling of the toxic water pollutants, requires practical actions of all levels of the hierarchical framework. Avoiding or minimizing use of both domestic and industrial based chemical products is an ideal strategy for reducing diffusion of toxic pollutants into our water resources. Also, improved farming techniques, for example, the use of organic manure and integrated pest management systems. This involves converting farms to use integrated pest management (IPM) techniques and organic farming methods. It depends on very effective preventive, monitoring, suppression, and avoidance methods based on an understanding of pest ecology. In order to provide healthy soil and habitat for organisms, this integrated pest management (IPM) and organic farming methodology heavily relies on ecologically oriented cultural and biological approaches. Environmental hazards from certain suppression strategies are improved by using appropriate mitigation techniques (Natural Resources Conservation service, 2014). Written plan and implementation of activities is required for high level IPM and it may include:

I. Techniques of prevention such as, cleaning equipment and gear when leaving an infested area, use of pest-free seeds, seedlings and transplants, scheduling of irrigation to avoid creating conducive environment for disease development.

II. Techniques of avoidance for instance, maintaining soil health and diverse plant communities, reducing crop susceptibility by nutrients levels management, use of pest resistant plant varieties, crop rotation, refuge management, mixed cropping, strip cropping, plant spacing and intercropping.

III. Monitoring techniques, for example, pest scouting, degree-day modeling, weather forecasting, soil and tissue sampling, use of economic thresholds. This helps in target suppression strategies and avoiding and/or minimizing routine preventative treatments. Scouting protocols for pests should include key natural enemies of each targeted species, as well as individual pests.

IV. Suppression techniques which may include cultural and biological control measures, managing by reducing pests' population or their impacts via minimizing risks to non-targeted organisms.

contamination of water through chemicals from industrial emissions can be reduced by use of cleaner production processes. Other interventions include recycling of chemical containers, proper treatment of hazardous waste and discarded products containing chemicals. This is to reduce leaching of toxic chemicals and solid waste buildups into water sources. A wide variety of technical solutions can be available for filtration of industrial processes involving chemical wastes to render them harmless (Kjellstrom et al., 2006).

2.3.1 Assessment

Water quality assessment is important in identification of water pollution. Therefore, in recent years water quality evaluation is considered critical, because freshwater is becoming scarce (Varol *et al*., 2012; Yan *et al*., 2015). For instance, biological water assessment has several benefits, not the least of which is the ability of benthic organisms to integrate different habitats and provide a clear indication of whether a certain combination of water quality analysis is appropriate. Second, impacts get absorbed over time, particularly for macroinvertebrates with longer lifespans. The majority of water pollution assessments are based on physical-chemical, heavy metal, and microbiological monitoring. Determining present situations and long-term trends is of utmost importance for efficient management. This is partially a reflection of how quickly data can be collected and analyzed, but it is mostly a result of the quantitative character of the result that is obtained (Sharma *et al*., 2016).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

The research region, sampling sites, sampling and sample analysis procedures, data gathering, and data analysis are all described in this chapter.

3.1.1 Description of the study area and sampling sites

For this study, twenty-two sampling sites were selected within Athi River and its tributaries based on possible pollution sources, accessibility and uses (**figure 3.1**). The sampling sites were distributed as flows: Nairobi River (Sites 6 - 10), Ngong River (Sites 11 - 14), Mathare River (Sites 15 - 17), Mbagathi/Athi River (Sites 1 - 5), Little Kiboko River (Site 22), Ruiru River (Site 20), Thiririka River (Site 21), Ruirwaka River (Site 18) and Kamiti River (Site19). Additionally, effluent from two waste water treatment plants (Kariobangi WWTP [Site 23] and Ruai WWTP [Site 24]) which discharge into the basin were included. Generally, the Kariobangi WWTP employs trickling filter technology and discharges its effluent into Nairobi River before confluence of its upstream tributaries. On the other hand, Ruai WWTP employs wastewater stabilization pond (WSP) technology and discharges its effluents into Nairobi River just after confluence with Ngong River.

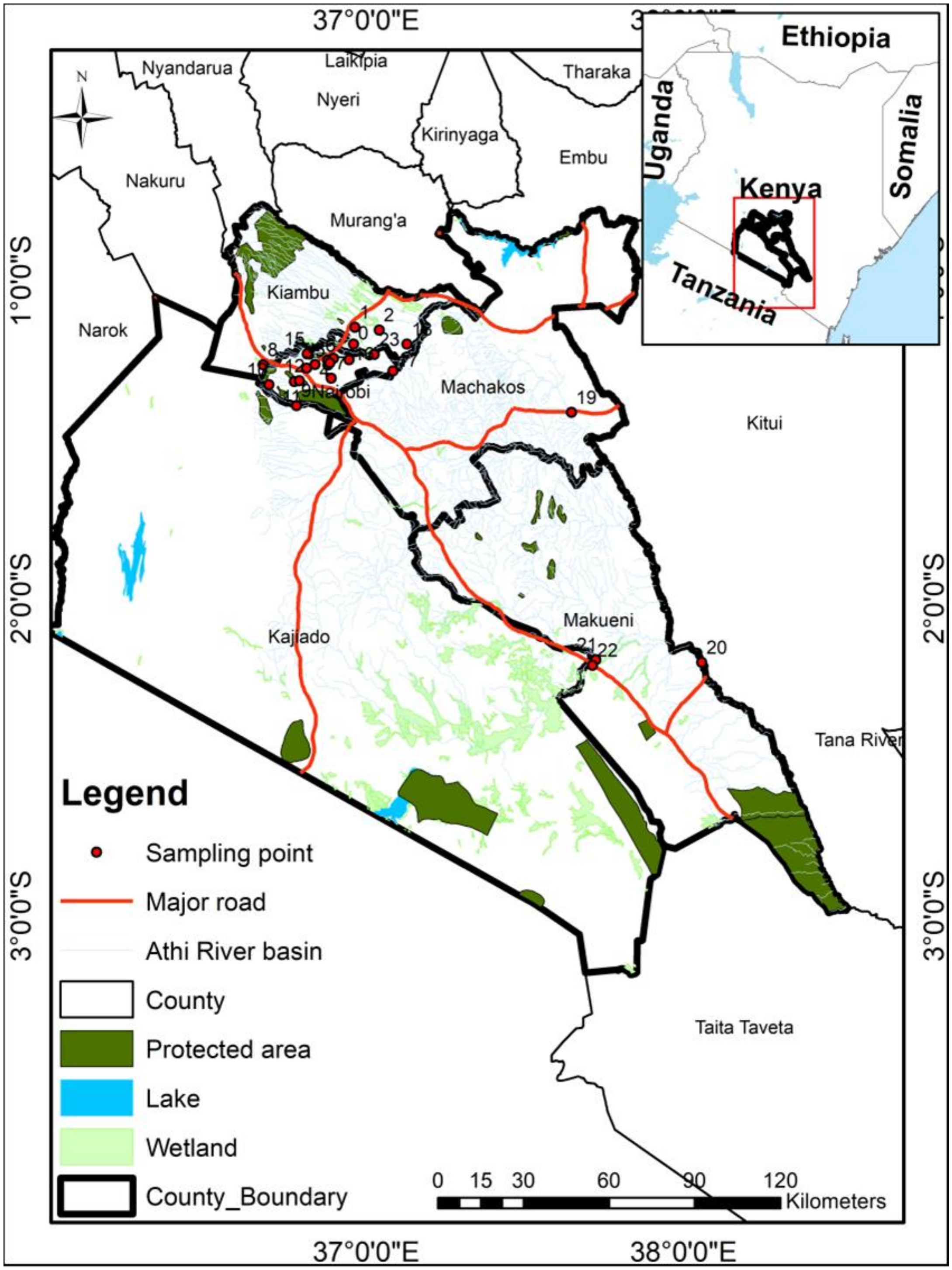

Figure 3.1: Map of sampling points within the Athi river Basin.

(Source: Author, 2022)

3.1.2 Sampling design, sampling and sample size

In this study, water was sampled from the selected sampling sites during three sampling campaigns between September 2020 and October 2021. Whereas the first sampling was done between (September-October 2020) and third sampling was between (September-October 2021 which is largely dry season, the second sampling campaign (May-June 2021) targeted the rainy season. Employing grab sampling technique, at each site, water was scooped in duplicate into pre-cleaned 2.0 L plastic bottles for physical-chemical parameters and heavy metals analysis. During the third sampling campaign, samples were taken in duplicate using 0.25 L sterilized glass vials for bacteriological examination. To avoid the entrance of floating objects during sampling, samples were taken at a depth of 10 to 30 cm below the water's surface with the open mouths of the bottles facing upstream of the flowing water. During the whole sampling campaign, 192 samples were taken in total, of which 144 were for physical-chemical and heavy metal analysis and 48 were for bacteriological examination.

Using a portable multiparameter kit, the water's temperature, pH, electrical conductivity (EC), and total dissolved solids (TDS) were all measured *in-situ* (HANNA instrument, HI 9813-6, Romania and EUTECH instrument, PC 650, Singapore). Before taking measurements, the equipment was calibrated each day to ensure accuracy. The samples were chilled at 4 °C while being transported to the WRA laboratory in an ice-cooled box for examination.

3.1.3 River flow measurement

To quantify the amount of water that flowed through a sampling site at any given time, river flow measurement was carried out by a hydrologist. Depending on practicality, different measuring techniques were employed including floatation, wading and/or Acoustic Doppler Current Profiler, ADCP and derivation from rating curves where river gauge levels existed. The river flow measurement is important in determining the contaminants load.

3.2 Laboratory analysis

Based on the Standard techniques for the study of water and wastewater, the chemical parameters were analyzed (APHA, 2017).

3.2.1 Chemicals and reagents

All of the chemicals utilized in this project were analytical-grade materials that were purchased from regional suppliers of lab supplies. When analyzing various parameters, the following substances and reagents were employed: Concentrated nitric acid, concentrated sulphuric acid, sulphuric acid with silver sulphate, COD indicator (ferroin), distilled water, potassium dichromate, standard ferrous ammonium sulphate (FAS), potassium antimony tartrate solution ($K(SbO)C_4H_4O_6.7H_2O$), ammonium molybdate solution $(NH_4)_6MO_7O_{24}.4H_2O$, ascorbic acid, io Standard solutions for iron, copper, zinc, lead, cadmium, and chromium, as well as for salmonella and shigella (S-S), are included.

3.2.2 Physical-chemical Parameters

3.2.2.1 Total suspended Solids

APHA 2540-D Total Suspended Solids Dried at 103–105°C was used to evaluate total suspended solids. In order to achieve a consistent weight, 1.2 m glass fibre filters (47 mm in diameter) were first oven dried at 105 °C. Weighing and recording the results of each filter was done in an analytical diary. Second, a sample volume of between 50 mL and 200 mL was filtered through the dry filters using a vacuum filtration device. Depending on the sample's degree of contamination, the analyst's expert judgment determined the amount that should be collected. The residue-containing filters were then oven dried at 105 °C for two hours before being weighed and recorded. Equation 4 was then used to calculate the TSS content, where A is the final weight of the filter paper and dried residue (mg), and B is the weight of the dried residue.

$$\text{TSS (mg/L)} = \frac{(\text{A}-\text{B})\times 1000}{\text{Sample Volume}} \text{ ....(Equation 4)}$$

3.2.2.2 Biochemical oxygen demand (BOD)

The BOD was measured using Respirometric method (APHA 5210-D). Depending on how polluted the water was determined by smell, colour, or conductivity of the sample, a volume of between 43.5 and 432 mL was measured into a clean brown BOD container. For example, 43.5 mL was used for samples suspected to have very high BOD whereas 432 mL of sample was used for less polluted samples. NaOH pellets were placed into the BOD breathers, fixed BOD bottles and corked using a manometric meters. The samples were then placed in an Oxitop-BOD incubator (WTW, Germany) under magnetic stirring at 20 °C for 5 days after which the results were recorded.

3.2.2.3 Chemical oxygen demand (COD)

COD was analyzed based on Closed reflux-titrimetric method, APHA 5220-C. An aliquot of each sample measuring between 0.1 to 2.5 mL was measured into a COD vial based on the level of contamination. Where less than 2.5 mL aliquot was measured, the sample was topped up to 2.5 mL using distilled water. Into the sample, 1.5 mL of digestion solution (0.016 M acidified $K_2Cr_2O_7$ containing 33.3 g/L of $HgSO_4$) was added. Additionally, 3.5 mL sulfuric reagent (concentrated sulfuric acid containing 5.5 g Ag_2SO_4 /kg H_2SO_4) was added into the mixture. In parallel, 2.5 mL of blank sample (distilled water) mixed with 1.5

mL digestion solution and 3.5 mL concentrated sulfuric acid was prepared. The samples and the blanks were placed in a COD thermoreactor (HANNA Instrument COD Reactor HI 839800) and digested at 148 ℃ for 2 hours. After digestion, the samples were chilled and titrated with 1,10-phenanthroline and iron (II) sulphate solution and ferroin starch indicator (0.1 M acidified ferrous ammonium sulphate, FAS). Equation 5 was used to calculate the COD content. Here, A, B, and M stand for the molarity and volume in mL of FAS utilized for the sample and blank, respectively.

$$\text{Calculation of COD} = \frac{(A-B)\times M\times 8000}{\text{sample volume used}} \quad \text{………………. (Equation 5)}$$

By boiling a solution of dichromate and sulfuric acid, the majority of electron donors (that is, organic matter) for COD were oxidized to carbon (IV) oxide and water. Refluxing a portion of the sample in a powerful acid known to contain an excess of potassium dichromate ($K_2Cr_2O_7$). The following reaction equation 6 transforms dichromate (chromate, VI, (Cr^{6+}), orange color) into chromate (chromate, III, (Cr^{3+}), green).

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O \text{ ------------------ equation (6)}$$

By using a titrimetric method, the remaining dichromate is back-titrated with ammonium iron (II) sulfate (ferrous ammonium sulfate (FAS)) to determine the amount of Cr2O72- consumed as illustrated in equation 7.

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \text{ ------------------ equation (7)}$$

Oxygen equivalents are used to determine the quantity of oxidized organic matter (Hu & Grasso, 2004).

3.2.2.5 Orthophosphates

Orthophosphates analysis was carried out based on ascorbic acid method, APHA 4500-P. About 50 mL of each sample was pipetted into different 100 mL beakers in duplicates. In parallel, a blank of 50 mL distilled water was also prepared in duplicates. Into both the samples and blanks, 8mL of combined reagent (5N H_2SO_4, potassium antimony tartrate, ammonium molybdate solution, 0.1 M ascorbic acid) was added followed by a drop of phenolphthalein indicator. The samples were left to stand for about 20 to 30 minutes. After that, samples' absorbance and orthophosphate concentration were measured using a UV-Vis Spectrophotometer (SHIMADZU UV mini-1240) with an 880 nm wavelength.

3.2.2.6 Nitrates

For nitrates analysis, ultraviolet-visible spectrometric screening method, APHA 4500-$NO_{3,}$ was applied. For each sample, 50 mL was measured and filtered using a filter paper into a beaker in duplicates. A blank of 50ml distilled water was prepared. Then, 1 mL of 1M HCL was added to each of the samples and blanks. Before being examined using a UV-Vis Spectrophotometer (SHIMADZU UV mini-1240, Japan) at a 220nm wavelength, the samples were allowed to settle for around 20 minutes. The samples were also examined at 275 nm for absorbance adjustment.

3.2.2.7 Sulphide

Iodometric Method The iodometric APHA 44500-S^{2-} sulphide technique was employed. A 50 mL flask was filled with between 5 and 20 mL of iodine, 20 mL of distilled water, and 2 mL of 6 N HCl. Depending on pollution extent of the sample, between 5 – 20 mL of sample was added into the mixture followed by three drops of starch indicator solution. Using 0.025 M sodium thiosulphate (freshly prepared), the samples were titrated until colourless solution was formed, each time recording burette readings. The sulphide concentration was determined using equation 8, where A, B, C and D represents the amount of iodine solution used, normality of iodine solution, volume of thiosulphate used and normality of thiosulphate solution used, respectively.

$$\text{Calculation of sulphide} = \frac{(A-B)\times(C-D)\times 16000}{\text{sample volume used}} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(Equation 8)}$$

3.2.2.8 Ammonia

Ammonia was analyzed using ammonia selective electrode method, APHA 4500-NH_3. Calibration of the ammonia selective electrode was done using 1ppm and 10 ppm standards of ammonium chloride stock solution respectively before analysis. After measuring 50 mL of each sample into a 100 mL beaker, 1 mL of 4 molar lithium chloride was then added. The materials were then examined using a United Kingdom-made JENWAY 3345 ion meter to provide measurements.

3.3 Heavy Metals

Atomic absorption spectroscopy (AAS), a common analytical technique, was used to evaluate the heavy metal concentrations of the water samples that had been collected. Care was taken when handling the samples to prevent contamination. Nitric acid was used to fully clean the glass, and it was then completely washed with distilled water. For the AAS instrumental analysis and blank determination, analytical-grade chemicals and reagents were employed. The following is a quick description of the methods for sample and standard preparation and analysis of metal.

3.3.1 Sample preparation for heavy metal analysis

Using Whatman 120mm diameter filter papers, 100 mL of each water sample was measured and put into a clean 250 mL conical flask. The samples were then digested by adding 5 mL concentrated HNO_3 and heating the mixture to a volume of between 15 and 20 mL on a hot plate within a fume chamber. The samples were then put into a 100 mL volumetric flask and filled with distilled water to the appropriate level.

3.3.2 Standards preparation

Iron, zinc, lead, copper, manganese, chromium, and cadmium mixed working standards of 0.1, 1.0, 2.0, and 2.5 mg/L were diluted serially from a 1000 ppm standard stock solution. The identical process used to make samples was used to prepare reagent blanks (APHA, 2017; Brandi & Wilson-Wilde, 2013).

3.3.3 Heavy metals sample analysis

The flame condition and absorbance were tuned, and the atomic absorption spectrophotometer (AAS SHIMADZU 7000, Japan) was put in place. Instrumental blanks (deionized water) and calibration standards were aspirated into the device following optimization. Calibration curves were plotted using the data from the calibration standards. The concentration of the target elements was then calculated from the linear calibration curves using the analysis of the procedure blanks and samples. For interference, the reading of blank samples was applied correctly according to Standard Methods for the Examination of Water and Wastewater (APHA, 1999, 2017).

3.4 Bacteriological analysis

The most probable number (MPN) approach, which is a common tool, was used for the analysis. It is the ideal method to employ for analyzing highly turbid or semi-solid materials, such as sediments or samples of sludge water (Ukpong & Udechukwu, 2015).

3.4.1 Inoculation and incubation of Salmonella and Shigella samples

The salmonella-shigella (S-S) agar medium was weighed and dissolved in 1000 mL of distilled water using around 60 grams. Once the suspension was consistent, it was heated to boiling to thoroughly dissolve the medium. It was chilled before being put onto sterilized petri dishes with a label that included the preparation date. A 1 mL of the sample water was then added, and then incubated at 37 °C for 24 hours (APHA, 1999, 2017; John Dekker, 2017; Ukpong & Udechukwu, 2015).

3.4.2 Counting of salmonella and shigella colonies

The culture was streaked on two selective medium after 24 hours of incubation at 37 °C in order to get individual colonies. These were Salmonella-Shigella (s-s) agar and XLD (xylose lysine deoxycholate) agar. Salmonella colonies with the typical red with a black center on XLD were recognized. On S-S agar, organisms with transparent colonies and black centers were recognized. Shigella appeared colourless, but salmonella had a black center and no colour (APHA, 2017; Ivera *et al*., 2010; Ukpong & Udechukwu, 2015).

3.4.3 Inoculation and incubation of total coliforms and *E. coli* samples

The MacConkey broth medium was properly mixed after being thoroughly dissolved in 1000 mL of distilled water. It was packaged in Durham tube-equipped screw-capped bottles. Following serial dilution of the samples, 0.1 mL of a dilution (10-1) was put onto five sterile petri plates with nutritional agar using a sterilized pipette. A fresh pipette was then used to deliver zero-point one milliliter (0.1 mL) of a different dilution (10-2) into a new set of five petri plates. The petri dishes were turned upside down and put in an incubator set to 30 °C within 48 hours (APHA, 1999; Feng *et al*., 2020; Sangadkit *et al*., 2012).

3.4.4 Counting of colonies

Colony counting took place after 48 hours of incubation at 30 °C. The plates with 30 to 300 colonies were counted using the colony counter technique under dim lighting. In order to calculate the bacterial load in the initial 25 grams of material using enumeration, the data were entered in a Microsoft Excel spreadsheet (APHA, 2017; Brugger *et al*., 2012; Sieuwerts *et al*., 2008).

CHAPTER FOUR

RESULTS

4.0 Results overview

The findings of this study were assessed and contrasted with drinking water quality criteria defined by the National Environment Management Authority (NEMA), the Kenya Bureau of Standards (KEBS), the East African Community Standards (EACS), and the Water Resources Authority (WRA) (NEMA). Tables 4.1 to 4.4 and figures 4.1 to 4.11 exhibit the results of the physical-chemical, heavy metals, and microbiological tests.

Table 4.1: *In situ* parameters (pH, temperature, conductivity) results ranges for the three monitoring seasons.

Sampling campaigns	pH	Temperature (^{o}C)	Conductivity (µs/cm)
1st	6.4 – 8.5	20.4 – 27.8	70 – 1750
2nd	6.7 – 8.5	18.5 - 26.7	62 – 1941
3rd	6.5 – 9.78	17.1 – 31.8	32 – 2005
Overall range	6.4 - 9.8	17.1 – 31.8	32 – 2005

Table 4.2: Results of physical-chemical parameters in rivers within the Athi river basin.

sampling campaigns	BOD (mg/L)	COD (mg/L)	TDS (mg/L)	TSS	sulphide (mg/L)	orthophosphate (mg/L)	ammonia (mg/L)	nitrate (mg/L)
1st	1 – 600	14 – 1000	43 - 1085	10 – 233	<1 – 6	7 – 18	0.31 – 52	ND - 36
2nd	1 – 460	14 – 800	39 - 1203	4 – 840	<1 – 72	0.1 - 12	ND – 180	4 – 44
3rd	1 – 640	32 – 3360	20 - 1243	5 – 495	<1 – 192	0.11 – 15	0.4 – 204	ND – 3
OVERAL RANGE	1 – 640	14 – 3360	20 - 1243	4 - 840	<1 – 192	0.1 – 15	ND – 204	ND – 44

4.1 Overall overview of physical-chemical parameters concentration in rivers within the Athi basin area

The overall total concentration of the physical-chemical parameters (ammonia, BOD, COD, nitrate, orthophosphate, sulphides, TDS and TSS) across the Athi River basin, from upstream till downstream before entry into the Indian Ocean (**Figure 4.1**). River upstream (Nairobi River at Kikuyu, Kamiti River at Kiambu, Thiririka River at Juja, Ruiru River at Thika road, Mbagathi River at Ngong road, Ngong River at Ngong forest, Ruirwaka at Lucky Summer and Nairobi River at Museum hill) had the lowest overall concentration of the physical-chemical parameter across the Athi river basin profile. Ruiru River at Thika road, Kamiti river at Kiambu and Thiririka river at Juja recording the lowest possible concentrations.

In the middle stage rivers recorded high concentration levels as compared to upstream rivers. Rivers at Outering area (that is, Nairobi River at Outering, Ngong River at Outering, Mathare River at Outering, Ngong River at Kibera Lindi bridge, Ngong River at Kangundo road, Nairobi and Mathare River at Gomongo) recorded highest concentrations.

Effluent treatment plants recorded the second highest concentrations after the middle stage. Kariobangi wastewater treatment plant recorded the highest concentration with Ruai waste water treatment plant recording considerably low concentrations.

Downstream rivers recorded relatively low concentrations but not lower than the upstream rivers. Nairobi river recorded the highest concentrations since it receives discharged treated water from the wastewater treatment plants. It was followed by Little Kiboko, Athi river at Wamunyu and Kibwezi.

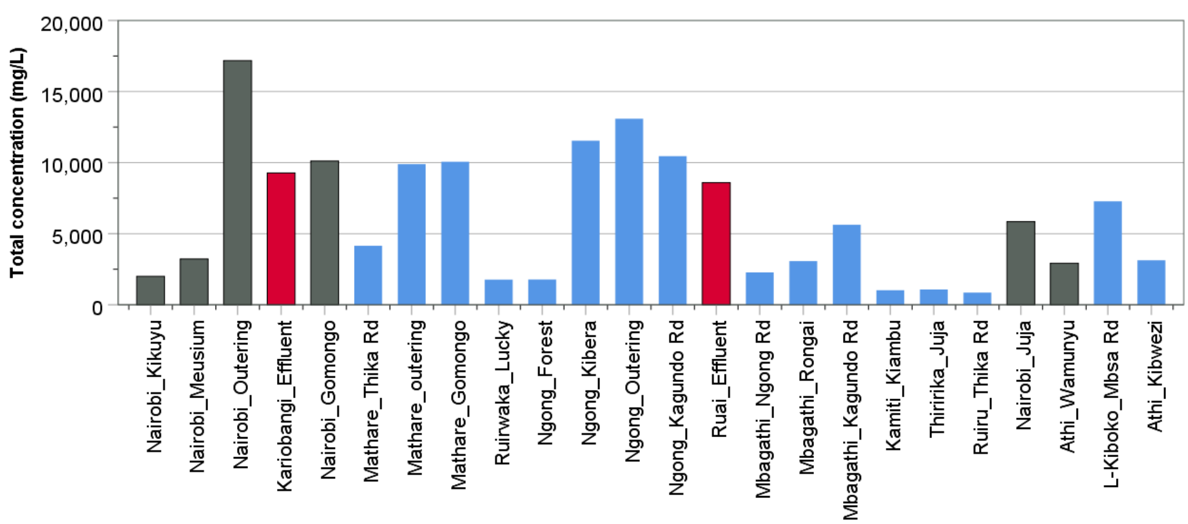

Table 4.1: Total concentration of physical-chemical parameters (ammonia, nitrate, orthophosphate, sulphide, TDS, TSS, BOD and COD) in river water and wastewater treatment plants (Kariobangi and Ruai) across the Athi river basin area profile.

4.2 Specific results of pollution indicators

These physical-chemical water quality pollution indicators were categorized into three specific groups which includes: Physical parameters, chemical parameters and nutrients as discussed below.

4.2.1 Physical parameters

4.2.1.1 Temperature

The observed temperature range was 17.1℃ to 31.8 ℃ overall, with readings of 20.4 ℃ to 27.8 ℃ in the first sampling, 18.5 ℃ to 26.7 ℃ in the second sampling, and 17.1 ℃to 31.8℃ in the third sampling (**Table 4.1**). In the first, second, and third sampling campaigns, respectively, a mean of 24.5±2.37 °C, 21.4±2.43 °C, and 22.8±2.26 °C, as well as a median of 25.25±2.37 °C, 20.6±2.43 °C, and 23.4±2.36 °C, were obtained (**Figure 4.2**).

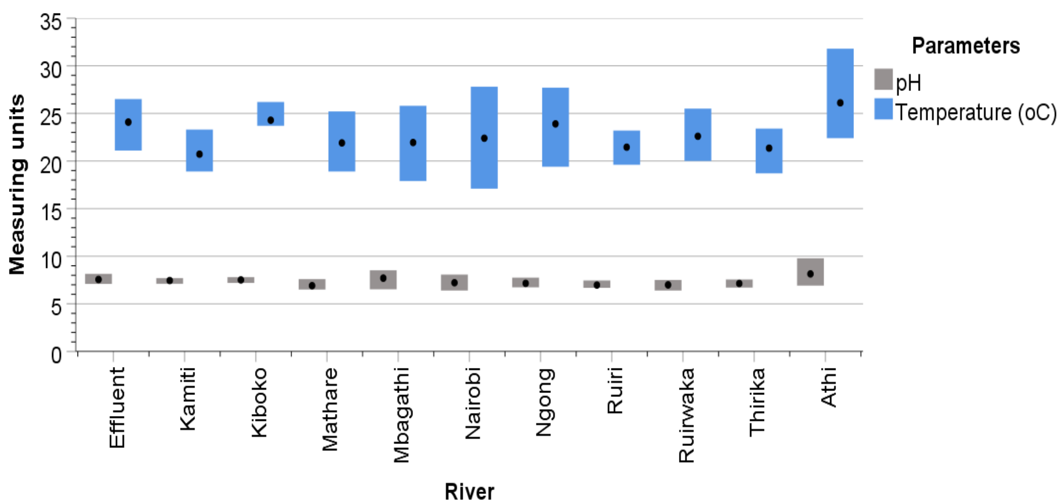

Figure 4.2: Hanging bar graph showing variation of pH and Temperature in rivers and wastewater treatment plants (Kariobangi and Ruai) within Athi River basin area.

4.2.1.2 Electrical Conductivity

The total conductivity range that was recorded ranged from 32 µs/cm to 2005 µs/cm. With a first sample range of 70 µs/cm to 1750 µs/cm, a second sampling range of 62 µs/cm to 1941 µs/cm, and a third sampling range of 32 µs/cm to 2005 µs/cm. A mean of 595±384 µs/cm, 644±444 µs/cm, and 732±483 µs/cm, as well as a median of 535±384 µs/cm, 543±444 µs/cm, and 732±483 µs/cm, (**Table 4.1**). High electrical conductivity was observed in Little Kiboko River, ranging from 1557 µs/cm to 1941 µs/cm. The third sample campaign (dry season) yielded the lowest conductivity of 32 µs/cm and the maximum conductivity of 2005 µs/cm in the Ruiru and Mbagathi rivers near Kangundo roads, respectively. The electrical conductivity for the upstream rivers was < 500 µs/cm, which is below the WHO guidelines of 1500 µs/cm for natural water, they include, River Kamiti, Mathare river at Thika road, Mbagathi river at Ngong road, Nairobi River at Kikuyu, Ngong River at Ngong forest, Ruiru river at Thika road, Ruirwaka river and Thiririka River. All wastewater treatment plants recorded EC values varying from 930 µs/cm to 1568 µs/cm. Ruai WWTP recorded in the range of 956 µs/cm to 1304 µs/cm while Kariobangi WWTP registered in the range of 930 µs/cm to 1568 µs/cm, (**Figure 4.3**).

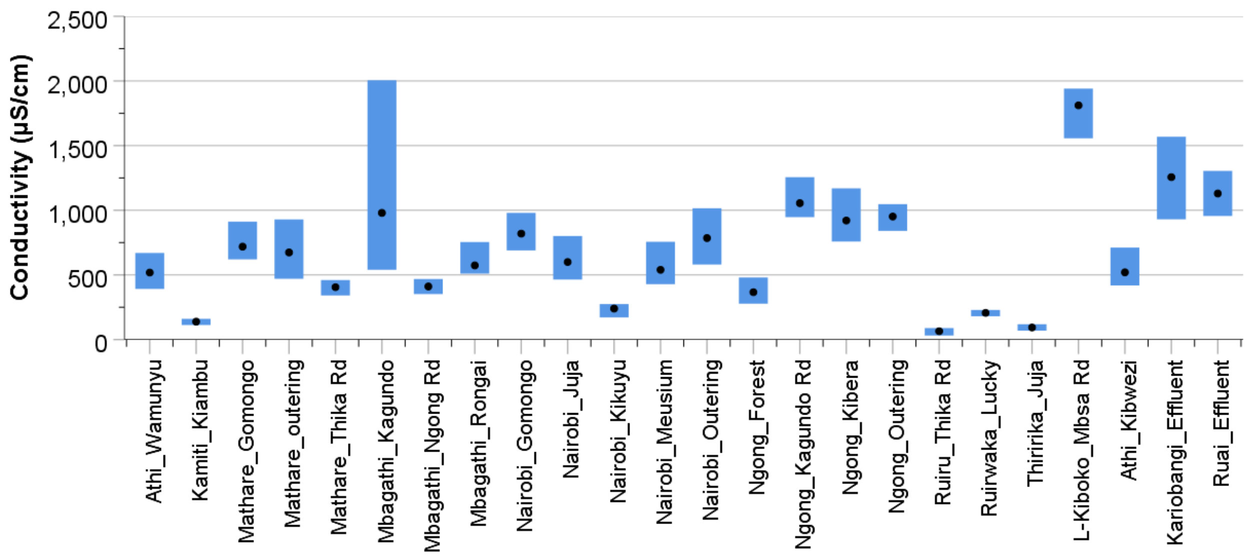

Figure 4.3: Electrical conductivity in rivers and wastewater treatment plants (Kariobangi and Ruai) within Athi River basin area.

4.2.1.3 Total Dissolved Solids (TDS)

TDS concentration was recorded in the range of 20 – 1243 mg/L. The first, second and third sampling campaigns concentrations ranged from 43 – 1085 mg/L, 39 – 1203 mg/L and 20 – 1243 mg/L, respectively, (**Table 4.2**). Mean concentrations of 369 mg/L, 400 mg/L and 454 mg/L with median concentrations of 33 mg/L, 337 mg/L and 454 mg/L were also recorded in the first, second and third sampling campaigns, (**Figure 4.4 and Figure 4.5**). Both the lowest and the highest concentrations of 20 mg/L and 1243 mg/L were recorded in the third sampling campaign (dry season). The lowest concentration of 20 mg/L was recoded at Ruiru river while the highest concentration of 1243 mg/L was recorded in Athi river at Kangundo road.

High TDS concentrations were also noticed in Little Kiboko river ranging from 965 – 1203 mg/L, with the lowest concentration of 965 mg/L recorded in the third sampling campaign (dry season) while the highest concentration of 1203 mg/L recorded in the second sampling campaign (wet season).

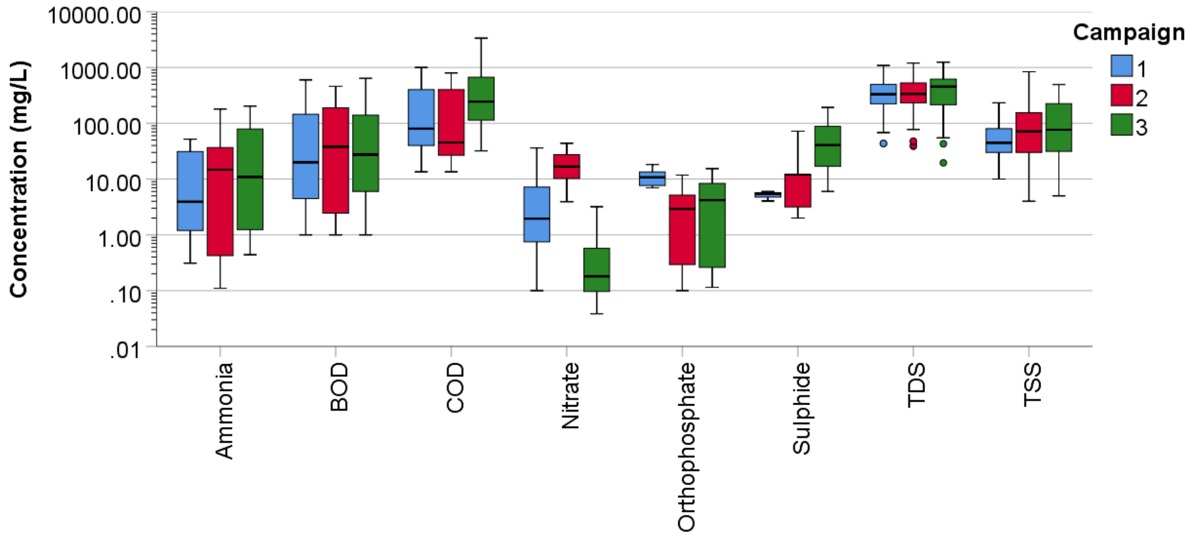

Figure 4.4: Seasonal concentrations and median of physical-chemical parameters in river water and wastewater treatment plants (Kariobangi and Ruai) within Athi River basin area.

4.2.1.4 Total Suspended Solids (TSS)

The registered TSS ranged between 4 – 840 mg/L (Table 2). With 10 – 233 mg/L, 4 – 840 mg/L and 5 – 495 mg/L recorded in the first, second and third sampling campaign, respectively. Both the lowest concentration of 4 mg/L and highest concentration of 840 mg/L were recorded in second sampling campaign (wet season) at Little Kiboko River and Nairobi River at Outering road.

The recorded concentration levels were above the acceptable levels of the East Africa Standards (EAS) acceptable limits of Nil limits for the natural portable water standards. Mean concentration of 65 mg/L, 120 mg/L and 133 mg/L, **Figure 4.5** and a median concentration of 45 mg/L, 72 mg/L and 77 mg/L, (**Figure 4.4**) were recorded in the first, second and third sampling campaigns, respectively.

Wastewater treatment plants recorded concentration ranging from 20 mg/L to 150mg/L. The lowest concentration of 20 mg/L was recorded in Ruai WWTP in the dry season (first sampling campaign). The highest concentration of 150 mg/L was recorded in Kariobangi WWTP in the wet season (second sampling campaign).

4.2.2 Chemical parameters

4.2.2.1 pH

The pH values in this study varied between 6.4 and 9.78, (**Table 4.1**). The lowest pH of 6.4 was recorded in the first sampling campaign in the dry season at Ruirwaka river and Nairobi River at Juja farm. The relatively high pH of 9.78 was recorded in the third sampling campaign of the dry season in Athi river at Kibwezi. The mean concentration of 7.32±0.48, 7.23±0.49, 7.44±0.67 while the median values were 7.35±0.48, 7.11±0.49 and 7.35±0.67 in the first, second and third sampling campaign, respectively. Ruirwaka River recorded the lowest pH of 6.4 with Athi River at Kibwezi recording the highest (pH 9.78).

On the other hand, all effluent from the waste water treatment plants (Kariobangi and Ruai WWTP) which discharge their treated waste water into Nairobi River then Athi river had pH of between 7.6 - 8.15 which are within the tolerance limits by the Kenya Bureau of Standards (KEBS) and National Environment Management Authority (NEMA) limit for natural portable water pH (6.0-9.0) for effluent discharge into the river system.

4.2.2.2 BOD and COD

The BOD concentration was recorded in the range of 1 – 640 mg/L, (**Table 4.2**). The highest BOD concentration of 640 mg/L was recorded in the third sampling campaigns at Nairobi River at Outering road. Nairobi River at Kikuyu and Ngong River at Ngong Forest recorded the lowest value of 1 mg/L. A mean concentration of 100 mg/L, 96 mg/L and 126 mg/L was recorded in the first, second and third sampling campaign respectively, (**Figure 4.5**).

On the other hand, COD concentration was recorded in the range between 14 – 3360 mg/L. For the first, second and third sampling campaigns concentrations were recorded in the range of 14 – 1000 mg/L, 14 – 800 mg/L and 32 – 3360 mg/L, respectively (**Table 4.2**). The highest concentration of 3360 mg/L was recorded in the third sampling campaign (dry season) and the low COD concentration of 14 mg/L in the first and second sampling campaign (dry season). The mean concentrations were 330 mg/L, 207 mg/L and 560 mg/L, (**Figure 4.5**). The median concentrations of 80 mg/L, 46 mg/L and 245 mg/L, respectively (**Figure 4.4**).

4.2.2.3 Sulphide

The overall range of concentration recorded was between <1 – 192 mg/L. The first, second and third sampling campaign recorded concentration range of <1 – 6 mg/L, <1 – 72 mg/L and <1 – 192 mg/L, respectively (**Table 4.2**). The highest concentrations of 192 mg/L with a mean concentration of 62 mg/L were recorded in the third sampling campaign (dry season). The least concentration of <1 was recorded in all the three sampling campaigns while the least mean concentration was in first sampling campaign, (**Figure 4.5**). On the other hand, the median concentrations recorded were 5.4 mg/L, 12 mg/L and 41 mg/L, (**Figure 4.4**).

The calculated average mean concentration of 33.69 mg/L was registered in the dry season (calculated from first and third sampling results). Hence, there was a high concentration of sulphides in the dry season than in wet season (second sampling campaign results) with a concentration of 16 mg/L. This indicated that the dry season concentration exceeded the wet season by a concentration factor of 2.08.

4.2.3 Nutrients

4.2.3.1 Ammonia and Nitrate

Ammonia was recorded in the range between ND – 204 mg/L. The highest concentrations of 204 mg/L of ammonia were recorded in the third sampling campaign while lowest concentration of ND (not detected) was recorded in the second sampling campaign. The range of between 0.31 – 52 mg/L, ND – 180 mg/L and 0.4 – 204 mg/L, (**Table 4.2 and Figure 4.4**). The mean concentrations of 15 m/L, 26 mg/L and 40 mg/L were also recorded in the first, second and third sampling campaigns, respectively (**Figure 4.5**). Ammonia was not detected in the second sampling campaign in Nairobi River at Kikuyu, Mbagathi River at Ngong road, Ruirwaka River, Thiririka River, Ruiru River and Kamiti River at Kiambu.

On the other hand, nitrates were also overally recorded in the range between ND – 44 mg/L, with the first, second and third sampling campaigns recording ND – 36 mg/L, 4 – 44 mg/L and ND – 3 mg/L, respectively (**Table 4.2 and Figure 4.4**) while the mean concentration of 8 mg/L, 20 mg/L and 0.61 mg/L were recorded in first, second and third sampling campaigns, **Figure 4.5**. Nitrates were also not detected in the first and third sampling campaigns. In the first sampling campaign it was not detected at Athi River at Kangundo road, Athi River at Wamunyu, Kariobangi WWTP. In the third sampling campaign it was detected in Mathare river at Outering road, Nairobi River at Gomongo, Nairobi River at outering road and Ngong River at Outering road. It was not detected in both first and third sampling campaigns in Mathare River at Gomongo and Nairobi River at Juja farm.

Similarly, the two wastewater treatment plants recorded ammonia and nitrate concentrations as follows; Ruai WWTP observed ammonia concentrations of 40 to 55 mg/L and nitrates concentrations of 0.2 to 19 mg/L, whereas Kariobangi WWTP recorded ammonia concentrations between 37 and 204 mg/L and nitrate concentrations between ND and 26 mg/L. This shows that the Kariobangi wastewater treatment facility reported both the low concentration of 37 mg/L of ammonia and ND for nitrates and the high concentration of 204 mg/L for ammonia and 26 mg/L for nitrates. In the dry season of the sampling campaign, ammonia concentrations were both lowest at 37 mg/L and highest at 204 mg/L (that is, first sampling campaign and third sampling campaign respectively). However, in both seasons, a low value of ND and a high one of 26 mg/L were observed (that is, first and second sampling campaign, respectively).

4.2.3.2 Orthophosphate

Orthophosphates were recorded in the range of 0.1. – 18 mg/L for the entire study period. The lowest concentration of 0.10 mg/L was recorded in the second sampling campaign while the highest concentration of 18 mg/L was in the first sampling campaign (**Table 4.2**). The highest mean concentrations of 10.79±3.13 mg/L, occurred in first sampling campaign (dry season). The lowest mean concentration of 3.36±3.29 mg/L was recorded in second sampling campaign. The third sampling campaign recorded a mean concentration of 5.03±4.63 mg/L, (**Figure 4.5**). Orthophosphates had a calculated average mean concentration of 7.91 mg/L from mean concentration of the first and third sampling campaign (dry season) and 3.36 mg/L second sampling campaign (wet season). The dry season concentration exceeded the wet season concentration by a factor of 2.35.

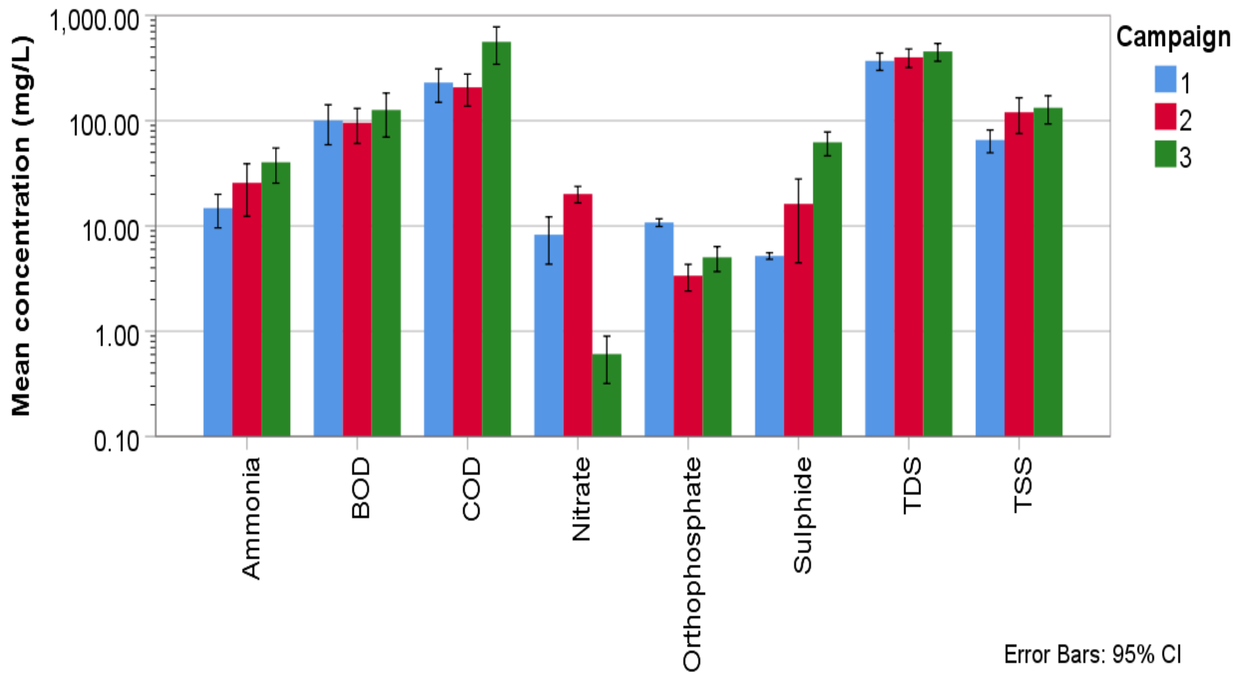

Figure 4.5: The mean concentration of physical-chemical parameters in rivers and wastewater treatment plants (Kariobangi and Ruai) within Athi River basin area.

4.3 Seasonal variations of physical-chemical parameters

Eight physical-chemical parameters were used to show the seasonal variation in the three-sampling campaign. These parameters included ammonia, BOD, COD, nitrate, orthophosphate, sulphides, TDS and TSS. Their overall concentrations distribution varied from <1 mg/L to 3360 mg/L, with <1 mg/L to 1085 mg/L, 0.1 mg/L to 1203 mg/L and 0.44 mg/L to 3360 mg/L recorded in the first, second and third sampling campaigns, respectively, (**Figure 4.6**). The least concentration of <1 mg/L was recorded in the first sampling campaign (dry season) for sulphides, COD, ammonia and nitrate. The highest concentration of 3360 mg/L was recorded in the third sampling campaign (dry season) for COD. Generally, there was no significant different between the concentration distribution of the first and the second sampling campaigns. This is clearly seen from the look of their close median concentration of 25 mg/L and 27 mg/L, respectively. Mean concentration distribution of these two (first and second) samplings campaign of 111 mg/L and 122 mg/L also illustrates this. On the other hand, the greatest variation difference of these physical-chemical characteristics was found during the third sample cycle. This is due to the fact that it measured a median concentration of 41 mg/L and a mean value of 177 mg/L (**Figure 4.6**).

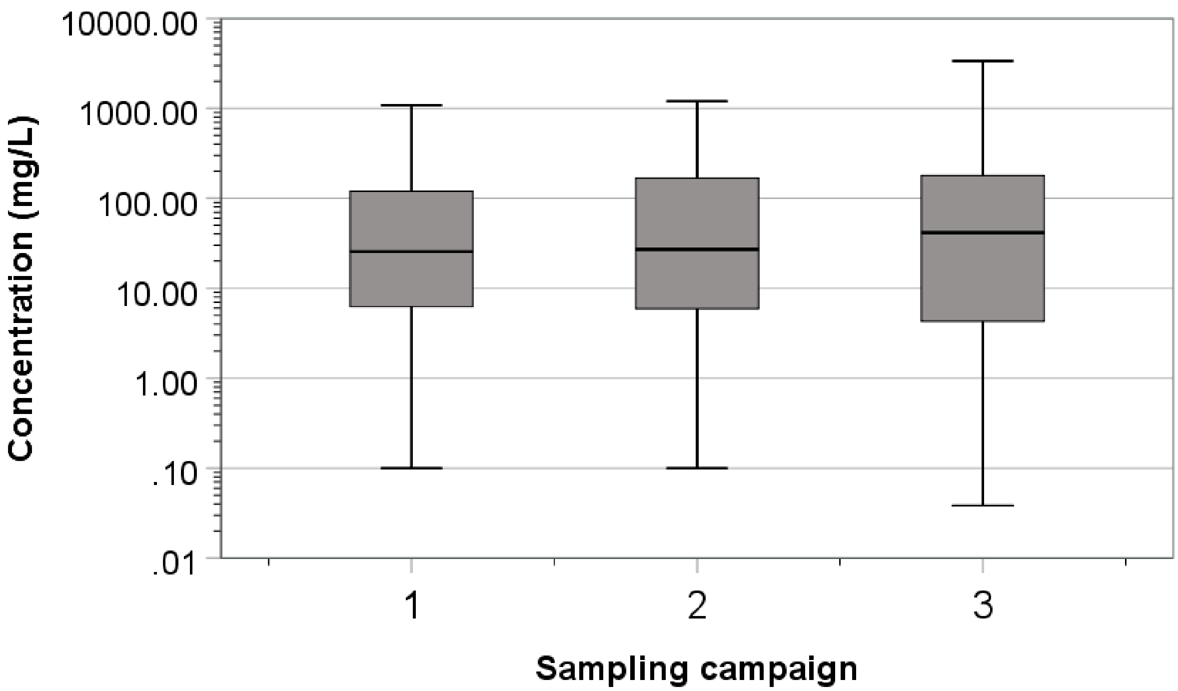

Figure 4.6: Seasonal variation of physical-chemical in rivers and wastewater treatment plants (Kariobangi and Ruai) within Athi River basin area.

4.4 Bacteriological results

Results of bacteriological assessment were tabulated as shown in table 4.3 and figures 4.7 and figure 4.8, respectively.

Table 4.3: Bacteriological assessment results in rivers within the Athi river basin area.

Parameter	MPN (counts/100 mL)
Total coliforms	$20 – 6.03\times10^{7}$
E. coli	$4 – 1.79\times10^{7}$
Salmonella	$1 – 1.01\times10^{2}$
Shigella	$1 – 1.11\times10^{2}$
Overall range	$1 – 6.03\times10^{7}$

4.4.1 Overall overview of bacteriological results

The overall total concentration of the bacteriological parameters (total coliforms, *E. coli*, Salmonella and Shigella) across the Athi River basin, from upstream till downstream before entry into the Indian Ocean, (**Figure 4.7**).

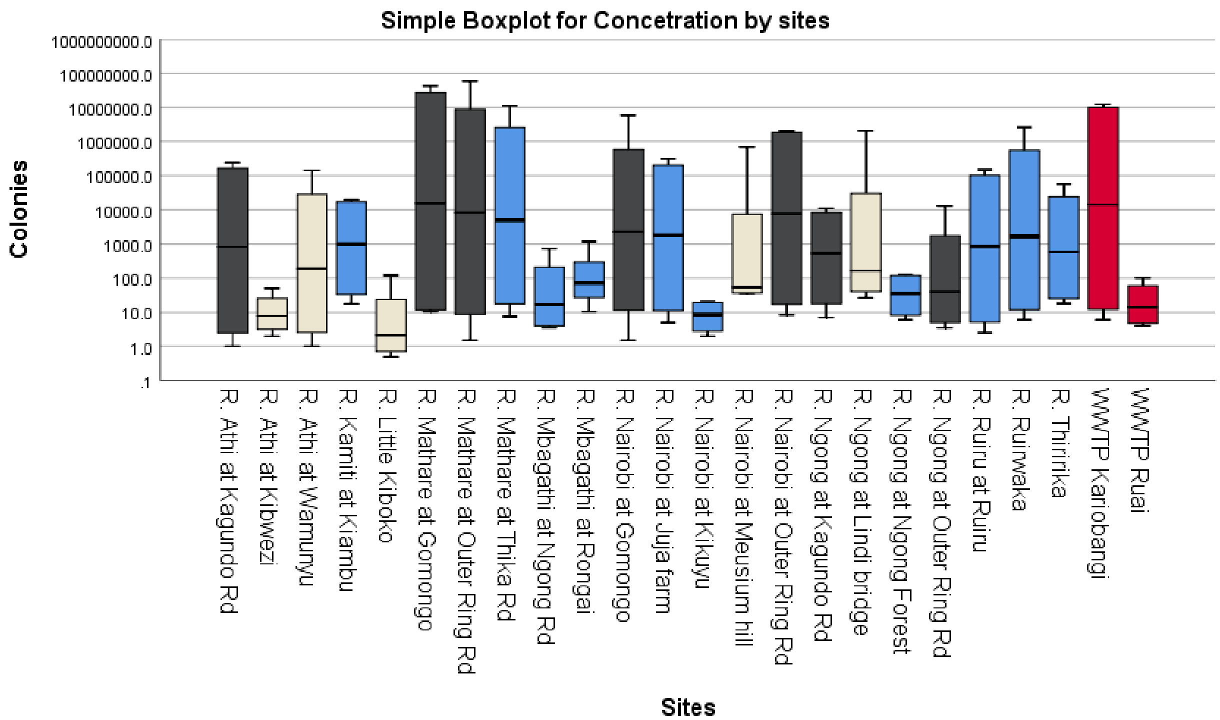

Figure 4.7: Concentration of bacteria in rivers water within Athi River basin area and wastewater treatment plants (Kariobangi and Ruai).

Upstream rivers recorded bacterial counts of between 2 – 2.66×10^5 counts/100 mL, presented in blue colour signifying low pollution in the Athi river basin. These rivers, include, Kamiti River at Kiambu, Mbagathi River at Ngong road, Mbagathi River at Rongai, Nairobi River at Kikuyu, Ngong River at Ngong forest, Ruiru River at Ruiru, Ruirwaka River and Thiririka River. Ruirwaka River recorded the highest bacterial counts of 5 – 2.66×10^5 counts/100 mL followed by Ruiru river at Ruiru 2 – 1.55×10^5 counts/100 mL, Thiririka river 17 – 5.7×10^4 counts/100 mL and Kamiti River 17 – 2.03×10^4 counts/100 mL, respectively.

Middle stream rivers presented in black colour signifying pollution hotspots area in the basin. These rivers include, Athi River at Kangundo road, Mathare River at Gomongo, Mathare River at Outering road, Nairobi at Gomongo, Nairobi River at Outering, Ngong

River at Kangundo road, Ngong River at outering, Nairobi River at Museum hill, Ngong River at Kibera Lindi bridge, and Mathare River at Thika road. Rivers at this stage recorded the highest bacteria counts with Mathare River at Outering road recording the highest count of 0 – 6.03×10^7 counts/100 mL, followed by Mathare River at Gomongo 9 – 4.44×10^7 counts/100 mL and Mathare River at Thika road bridge 6 – 1.986×10^7 counts/100 mL. Nairobi River at Gomongo recorded 1 – 6.89×10^6 counts/100 mL, while Ngong River at Lindi bridge Kibera recorded 23 – 2.42×10^6 counts/100 mL and Ngong River at Outering recorded 8 - 2.42×10^6 counts/100 mL.

Effluent from two waste treatment facilities Ruai and Kariobangi wastewater treatment plants (WWTP) were also analyzed. These WWTP discharge into the basin and they are presented in red colour to signify point source of pollution. Kariobangi WWTP recorded the highest bacteriological concentrations of 6 – 1.2×10^7 counts/100 mL while Ruai WWTP recorded considerably low bacterial concentrations of 4 – 1.01×10^2 counts/100 mL.

Downstream rivers presented in grey colour recorded relatively low concentrations but not lower than the upstream rivers presented in blue colour. Nairobi river at Juja farm recorded the highest number of bacteria of 4 – 3.4×10^5 counts/100 mL. Salmonella and shigella had the lowest bacterial counts, with an average of 5 counts/100 mL and 25 counts/100 mL, respectively, whereas total coliform and *E. coli* had the highest numbers at 1.285×10^5 and 3.15×10^5 cfu/100mL, respectively.

4.4.2 Individual distribution of bacteria genuses within the Athi river basin area

The overall concentration of bacteria in the Athi River basin was in the range of 1 – 6.03×10^7 counts/100 mL, (Table 3). Total coliforms recorded the highest concentration according to total number counts in the range of 20 – 6.03×10^7 cfu/100 mL. *E. coli* followed closely in the range of 4 - 1.79×10^7 cfu/100 mL. While on the other hand, Salmonella and Shigella both showed a narrow distribution range between them with concentration range 1 - 1.01×10^2 counts/100 mL and 1 – 1.11×10^2 counts/100 mL, respectively, (**Figure 4.8**).

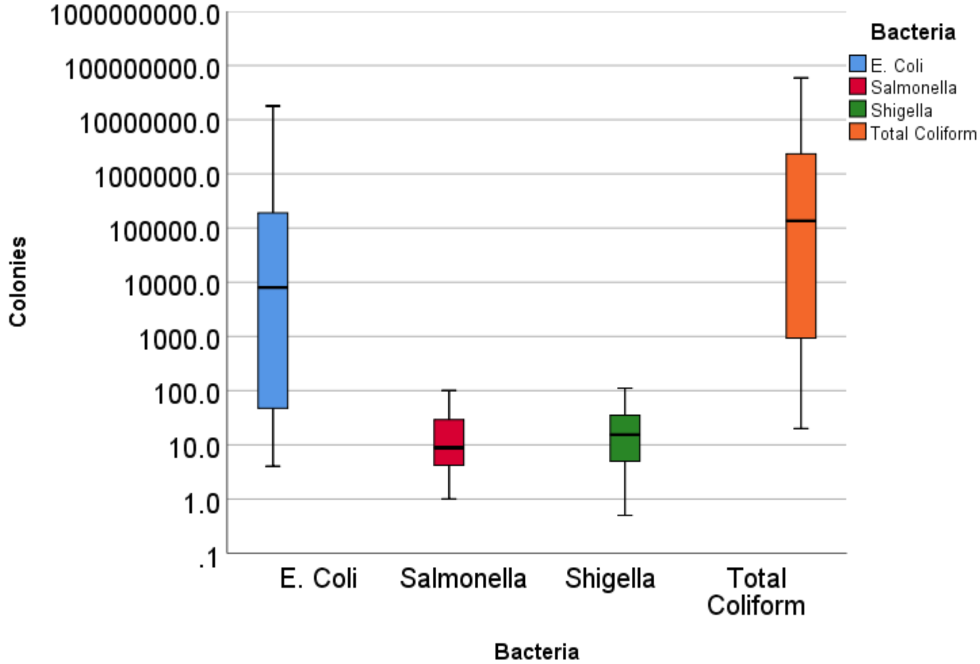

Figure 4.8: Individual distribution of bacterial genuses in rivers and wastewater treatment plants (Kariobangi and Ruai) within Athi River basin area.

4.5 Heavy metals

Heavy metals results were tabulated as indicated in **table 4.4** and **figure 4.9,** to **figure 4.11**, respectively.

Table 4.4: Heavy metals results in the three monitoring seasons.

Sampling campaigns	Cd (mg /L)	Cr (mg/ L)	Cu (mg/ L)	Fe (mg/L)	Mn (mg/L)	Pb (mg/L)	Zn (mg/L)
1st	ND	ND	ND	0.02 – 7.6	ND – 3.1	ND – 0.6	ND – 3.4
2nd	ND	ND	ND	0.01 – 7.5	0.001 – 4.3	ND – 0.02	0.01 – 3.4
3rd	ND	ND	ND	0.01 – 4.04	ND – 3.1	ND – 0.7	ND – 2.1
Range per sampling campaign	ND	ND	ND	0.01 – 7.6	ND – 4.3	ND – 0.7	ND – 3.4
Overall range	ND – 7.6 mg/L						

4.5.1 Distribution of Heavy metals in rivers water within Athi river Basin area

Upstream rivers recorded relatively low heavy metals concentration. These rivers include, Kamiti at Kiambu, Mbagathi at Ngong road, Mbagathi at Rongai, Nairobi at kikuyu, Ngong at Ngong forest, Ruiru at Ruiru, Ruirwaka and Thiririka River. Mbagathi at Ngong road and Ngong at Ngong forest recorded the least. Midstream rivers which recorded the highest concentration of metals as compared by the upstream, followed by downstream and effluents. These rivers include: Athi River at Kangundo road, Mathare River at Gomongo, Mathare River at Outering road, Nairobi River at Gomongo, Nairobi River at Outering, Ngong River at Kangundo road, Ngong River at Outering, Nairobi River at Museum hill, Ngong River at Kibera Lindi bridge and Mathare River at Thika road. Ngong River at Outer ring recorded the highest. Downstream rivers recorded concentrations which had no significant difference with those of the upstream rivers. These rivers include Nairobi River at Juja farm, Athi river at Wamunyu, Athi river at Kibwezi and little Kiboko. Wastewater treatment plants recorded same concentration of heavy metal but in the same range as those of upstream rivers (**Figure 4.9**).

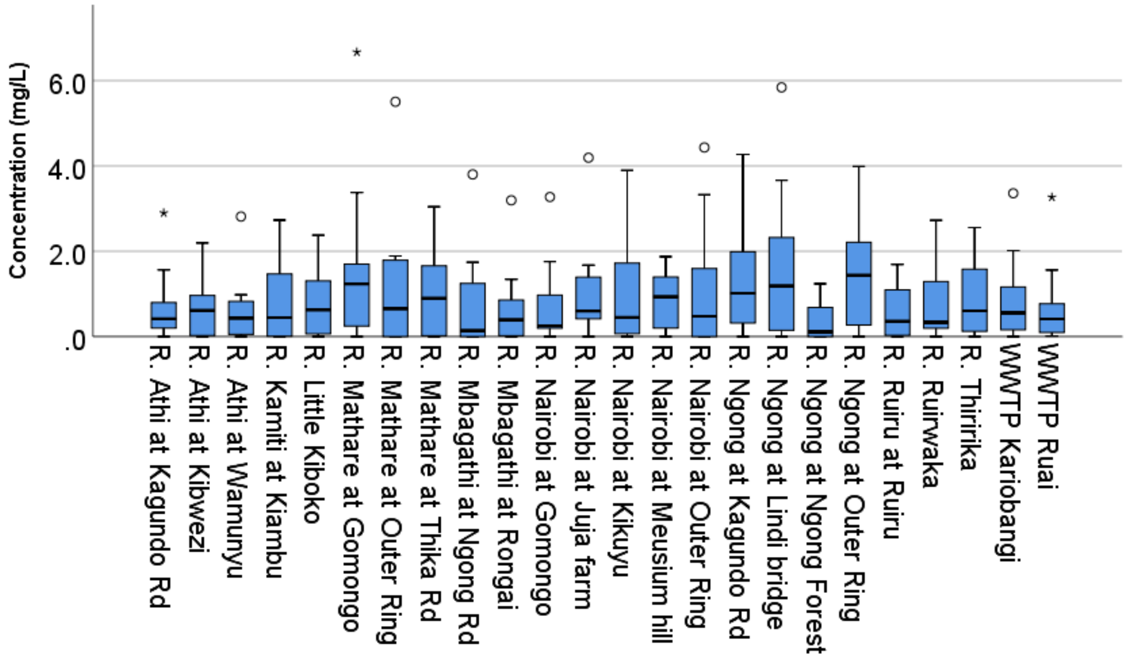

Figure 4.9: Overall heavy metal concentration in rivers water within Athi River basin area.

4.5.2 Heavy metals concentration in Athi river basin area

Metals were recorded in the range varying from ND to 7.6 ppm, **Table 4.4**. chromium, Cr, cadmium, Cd and copper, Cu, were not detected while iron, Fe, recorded in the range of 0.01 ppm to 7.6 mg/L, manganese, Mn, was recorded in the range ND to 4.3 mg/L, lead, Pb, in the range of ND – 0.7 mg/L and zinc, Zn, in the range of ND – 3.4 mg/L (**Figure 4.10**).

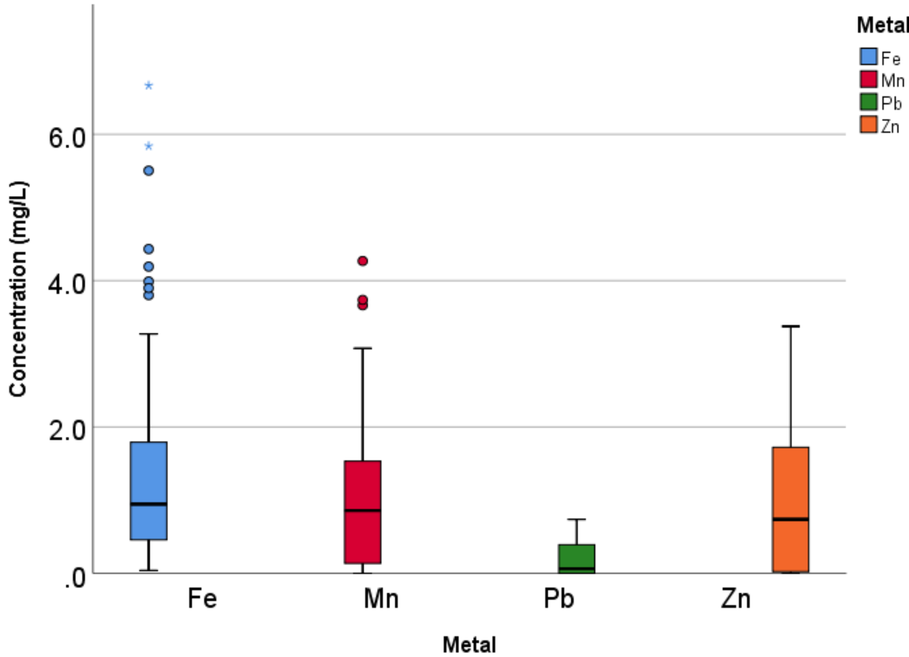

Figure 4.10: Overall heavy metal (iron, manganese, lead and zinc) concentration levels in rivers within Athi River basin area.

4.5.3 Seasonal Variation of heavy metals

First sampling campaign recorded the highest metal concentration in the range of ND – 7.6 mg/L, with the second and third sampling campaign recorded ND – 7.5 mg/L and ND – 4.04 mg/L (**Figure 4.11**).

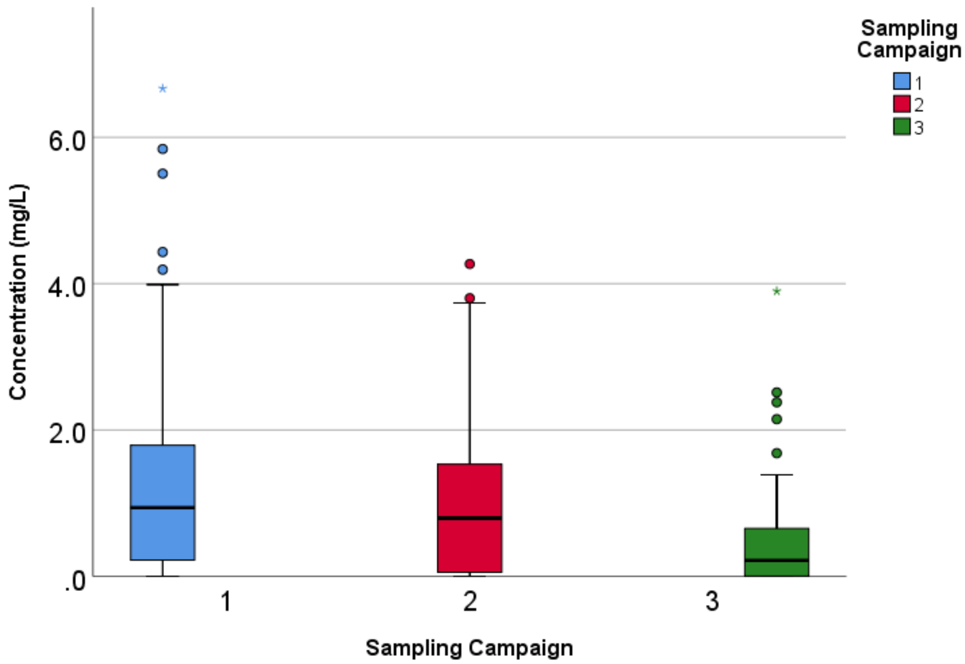

Figure 4.11: Seasonal variation of heavy metal concentration in rivers and wastewater treatment plants (Kariobangi and Ruai) within Athi River basin area.

CHAPTER FIVE

DISCUSSION

5 Physical-chemical parameters

5.1 Overall overview of physical-chemical parameters concentration in rivers within the Athi basin area

River upstream had the lowest overall concentration of the physical-chemical parameter across the Athi river basin profile. Ruiru River at Thika road, Kamiti river at Kiambu and Thiririka river at Juja recording the lowest possible concentrations. This indicated there was very minimal pollution experienced in this region.

In the middle stage rivers recorded high concentration levels as compared to upstream rivers. This was majorly due to high pollution by organic matter from both the industrial and domestic wastes. For example, there was a direct discharge of raw sewage into the river at Ngong river at Lindi bridge. This was due to poor sanitation of these areas.

Effluent treatment plants recorded the second highest concentrations after the middle stage, pointing out treatment plants as point sources for surface water pollution as per the results of water quality parameters analyzed (that is, BOD and COD).

Downstream rivers recorded relatively low concentrations but not lower than the upstream rivers. However, Nairobi River recorded the highest concentrations since it receives discharged treated water from the wastewater treatment plants. This elevated concentration levels of the parameters analyzed. It was followed closely by Little Kiboko River which is as a result of nature of the underlying bedrocks over which its water flows. Athi river at Wamunyu and Kibwezi recorded considerably same concertation of these parameters because this two sampling points lied within the same river profile. Therefore, indicating that there was a complete water mixing thus even distribution of their contents

5.1.1 Physical parameters

5.1.1.1 Temperature

The highest temperature and the lowest temperature were recorded in the third sampling (dry season-October, 2021) which are 17.1 ^{o}C and 31.8 ^{o}C. They were recorded in Nairobi River at Kikuyu (Nyongera) which were sampled in early hours of the morning when the sun was not too hot and Athi river at Kibwezi which was sampled in the afternoon when the sunshine was overhead and too hot. These water temperatures were sampling time dependent, that is, the time of the day when the sampling was done and also on the season and the temperature of effluent which are discharged into the river system.

All effluents from the waste water treatment plants (Kariobangi and Ruai waste water treatment plants) had temperature range of between 21 ^{o}C - 26.5 ^{o}C. This temperature range was within the KEBS, WASREB and NEMA tolerance limit for natural surface water temperature of <3 ^{o}C of the ambient water body temperatures for effluent discharge into the river system.

Biological activities and growth are majorly influenced by temperature, governing the kind of organisms that can live in different surface water sources such as river and lakes.

All aquatic flora and fauna, such as, fish, insects, phytoplankton and zooplanktons have a preferred temperature for survival. Temperature fluctuations from favourable or preferred range to too far above or below range leads to reduction in species of some aquatic organisms due to death, migration due to increased stress hence reduced reproduction until finally there are none. High temperatures causes warm water thus reduces the vigor of cold-water fish species, leaving them more vulnerable to illness and parasites, the organisms move to areas with favourable temperatures. (Steven, 2017).

Given that it affects water chemistry, temperature is one of the most crucial factors in the examination of physical-chemical parameters. At greater temperatures, chemical reactions often proceed more quickly. For instance, greater groundwater temperatures cause more minerals from the underlying rock to dissolve, increasing the water's electrical conductivity (U.S. Geological Survey, 2019). When taken alone, water temperature has an impact on the biological activity and metabolic rates of aquatic species. As a result, it affects the aquatic life's preferred environments. Warmer temperatures favor some creatures, especially aquatic vegetation, whereas colder streams are preferred by fish like trout and salmon. Metabolic rates and water temperature have been found to be directly correlated in studies. Many cellular enzymes become more active at higher temperatures, which causes this. A 10 °C increase in water temperature will about double the pace of physiological function for the majority of fish. Some animals can manage this rise in metabolic rate better than others. In most animals, increased metabolic function may be shown in respiration rates and digestive reactions. Greater oxygen consumption results from increased respiration rates at higher temperatures, which can be harmful if rates are raised for an extended length of time. Additionally, enzymes might start to break down at temperatures above 35 °C, decreasing metabolic activity. High water temperatures also have an impact on aquatic species as well as enhance the solubility and toxicity of particular substances like ammonia as well as heavy metals like cadmium, zinc, and lead. In addition to making harmful substances more soluble, water temperature can affect an organism's tolerance limit. Those above 25 °C result in much greater zinc mortality rates than temperatures below 20 °C. This happens because rising water temperature causes an increase in tissue permeability, metabolic rate, and oxygen consumption (Fondriest, 2014c).

5.1.1.2 Electrical Conductivity (EC)

The capacity of water to carry electrical current is measured by its conductivity. The concentration of ions in water has a direct impact on the EC of the water (electrolytes, that is, cations and anions). The water's conductivity increases with the concentration of these electrolytes in it. Likewise, the fewer the electrolytes present in the water, the less conductive the water is. EC recorded in rivers in this study were in compliance with the WRA and EAS acceptable limits of ≤2500 µs/cm for natural portable water. Sila, (2019) also reported a conductivity of 805 µs/cm at Athi River which was within the range reported in this study. The low electrical conductivity of 32 µs/cm in Ruiru river is perhaps attributed by minimal to almost non-domestic waste pollution from agricultural and industrial activities in the area and its environs.

High electrical conductivity varying from 540 µs/cm to 2005 µs/cm in Mbagathi river at Kangundo road was highly attributed by the high level of organic matter pollution. These pollutants gained entry into the river ecosystem from raw domestic waste as a result of burst sewer lines. This area is an upcoming urban centre but it lacks proper sanitation facilities and safe secure dumping site for domestic wastes. These organic compounds are broken down by bacteria in the water. As part of their metabolism, oxygen is used to oxidize organic carbon molecules, which releases carbon dioxide (CO_2) after the potential energy held in these compounds' chemical bonds has been released (burned). This CO_2

quickly dissolves to generate carbonic acid (H_2CO_3), bicarbonate ions (HCO_3^-), and carbonate ions (CO_3^-), in variable amounts, depending on the pH of the water. The "new" acid gradually reduces the pH of the water while the "new" ions elevate the TDS and subsequently the EC of the hypolimnion. In essence, they "consume" organic molecules in a manner similar to how we do, emitting CO_2 (Sururi, M. R., Roosmini, D., and Notodarmojo, 2018).

On the other hand, Little Kiboko River is dominated by spring water (groundwater) which contains higher salt concentration. Therefore, it recorded high electrical conductivity varying from 1557 µs/cm to 1941 µs/cm. The high conductivity in the little Kiboko river was as a result of its origin from Kiboko wetland system. This system was formed by surface runoff, springs from rain seepage, surrounding hills mist, permanent swamps and lake Amboseli. Fine alkaline sediments with high calcium and magnesium content have been accumulated over many years in the Amboseli lake basin by seasonal runoff from the watershed, including sediments brought downstream by the Namangan River. When there has been a lot of rain, the Namangan River can contain some shallow water, but the majority of the year it is still a hostile wasteland. Because of the high rates of evaporation and high soda ash deposits in the water caused by the high temperatures in this location due to the low altitude, this leads to high concentrations of total dissolved solids. (Nyingi *et al*., 2013).

The middle stream rivers registered electrical conductivity from 429 to 1256 µS/cm. These rivers traverse the informal settlements dwellings of Nairobi, for example, Kibera, Mathare, Ngomongo and the Nairobi industrial area. Poor drainage systems and sanitation facilities in these regions contributes mostly to domestic and industrial waste pollutants containing anions or cations like sodium, magnesium, and iron, as well as inorganic dissolved solids like nitrate, sulphate, and phosphate (Nyandwaro, 2017). These pollutants gain entry into these rivers through introduction of both raw industrial wastes from the industries within industrial area and raw domestic effluents from these informal settlements into the river basin. Presence of Dandora dumping site is another catastrophic pollution contributor, largely to Nairobi and Mathare Rivers at Ngomongo before confluence with Ruirwaka river. This is due to seepage of contaminants especially during the rainy season when the wastes are rained on, they hold water for quite a long time then they drain the water through underground seepage and surface run-off into the rivers. This increases the concentration of the electrolytes thus the electrical conductivity of the river water results to be above the WHO limits of 1500 µs/cm for natural water.

The most interesting thing here was that, downstream Athi River at Wamunyu recorded conductivity varying from 391 µs/cm to 670 µs/cm while Athi River at Kibwezi recorded conductivity varying from 505 µs/cm to 711 µs/cm. This difference was as a result of Little Kiboko River joining main Athi river just between Athi River at Wamunyu and Athi River at Kibwezi but closer to Kibwezi. The entry of Little Kiboko River which contained high concentration of dissolved solids since it had high soda ash deposit in water thus high concentration of calcium and magnesium.

For the effluent samples the conductivity of Ruai waste water treatment plant varied from 956 µS/cm to 1304 µS/cm. This electrical conductivity was within the tolerable limits of the NEMA and KEBS of 2500 µS/cm for discharge into surface water resources. On the other hand, Kariobangi WWTP recorded conductivity varying from 930 µS/cm to 1568 µS/cm. The low conductivity of 930µS/cm was recorded in the first sampling campaign (dry season) while the highest conductivity of 1568µS/cm was recorded in the second sampling campaign (wet season). The highest conductivity value was slightly above the NEMA and KEBS tolerable limits for the treated wastewater discharge into the river system.

Therefore, water's electrical conductivity is crucial because it shows the quantity of dissolved solids in a body of water. Small amounts of dissolved particles can increase the electrical conductivity of water; larger levels of dissolved solids lead to greater conductivities (Rahmanian *et al*., 2015; Sensorex, 2020; Wu *et al*., 2021).

5.1.1.3 TDS

TDS was measured in this study's surface water bodies in real-time by monitoring its surrogate-specific conductance. The TDS, which has a direct relationship with conductivity showed similar pattern as electrical conductivity. The recorded TDS concentration of range between 20 - 1243 mg/L across the river basin were in compliance range of the EAS acceptable limits of below 1500 mg/L for natural portable water. Total dissolved solids in water are often calculated as the sum of all dissolved organic and inorganic materials, that is, they are minute quantities of organic materials and inorganic minerals and salts that are in solution in water.

The rivers with high TDS were as a result of high dissolution of minerals in them. These minerals could have originated from a number of sources which include both agricultural land use, urban surface runoff and human activities. Agricultural cultivation in the riparian areas involves application of inorganic compounds, for example, nitrates, sulphates and phosphates for instance., NPK fertilisers. These might have leached into the river ecosystem there for dissociating and releasing either nitrate, phosphates and potassium ions into the water. The presence of these anions and cations in water increase the conductivity of water which in turn increase the TDS. Also, urban runoffs can bring in water which contain inorganic chemical for example., alkali metals-based salt chemicals into the river system. They in turn dissociate in water to give metal ions (cation and anions) which then elevates the conductivity hence high TDS. Also, wastewater discharges from both industrial and domestic wastewater treatment plants could have led to high TDS (Safe Drinking Water Foundation, 2017).

It was noted that TDS levels in the wet season was highly reduced due to dilution of the dissolved minerals and salts and small amounts of organic matter. This could have been attributed by the incoming rain water through surface runoff. Heavy rains lower a body of water's TDS by lowering the salinity content. Flooding occurs when there has been a lot of rain or another significant weather event. Depending on the water body and nearby soil, it may have an impact on TDS. Due to the diluting effects of the entering water, TDS often decreases overall during the rainy season in regions with distinct dry and wet seasons. As a result, the season's total TDS is reduced. When water first enters a floodplain with nutrient-rich or mineralized soil, TDS levels frequently increase. As a result, previously dry salt ions may enter the solution as it is flooded, raising the water's TDS (Arefin T. M. *et al*., 2016; Fondriest Environmental , 2014; Kassegne & Leta, 2020;).

Similarly, for the high TDS values of 965 – 1203 mg/L recorded in the Little Kiboko River were as a result of minerals from the bedrock of this river. This is because its source is a spring aquifer (groundwater) which contains high levels of fluorides, hardness, high iron and manganese contents (Ministry of Water and Irrigation, 2008; Nyingi *et al*., 2013). The highest concentration of 1203 mg/L was recorded in the second sampling campaign (wet season) despite the heavy rains and more incoming water due to surface runoff. This indicated that the increase in the water volume in the spring source river increase the dissolution of salts from the underlying rocks into the river water. Also, agricultural fertilisers from the adjacent Kenya agricultural and livestock research organisation (KALRO) through which the river traverse through might have had an impact in elevating the TDS concentrations.

TDS is often closely related to salinity, conductivity, alkalinity and hardness which are measures of the water mineral content. So, the more TDS in the water, the higher the hardness and turbidity which are measures of water clarity (Dobroshi, 2020; Sarwa *et al*., 2019).

The negative effects of high TDS include water that has a salty or brackish and is caustic due to the high concentration of dissolved ions. Additionally causing rusting in iron pipes for instance, in power generation firms, this reduces the efficiency of hot water heaters and steam-generating boilers. There are also expensive water treatment expenses, mineral build-up in plumbing pipes, discoloration, corrosion, and restricted irrigation usage. Prolonged exposure to drinking water containing high TDS>500 mg/L can cause kidney stone (Sharma & Bhattacharya, 2017). However, most freshwater animals, like bugs and fish cannot tolerate high TDS because they are not adapted to saline (salty) water like marine animals such as fish (Data Stream, 2021)

5.1.1.4 TSS

High TSS values of 4 – 840 mg/L was recorded. High amounts of TSS were mainly recorded at stations that are associated with informal settlement, a reflection of the impact of solid waste dumping in such areas. Additionally, river bank erosion that was observed at some of the sampling sites (for instance, Nairobi River at Kikuyu) during sampling can explain some of the observations. Notably, high TSS values were also observed at sites (for instance, Nairobi River at Kikuyu and Juja Farm) where farming activities are carried out in the riparian land, a sign of farm erosion. Similarly Mbui *et al*., (2016) also reported significantly higher concentrations of TSS in Nairobi River of between the range of 140 – 310 mg/L. These TSS values range was high above the EAS and WASREB recommended levels of Nil (ND) in natural portable water.

Average TSS mean value of 38.5 mg/L in the dry season discharged from the WWTP was calculated. This was done by summing the value recorded in the first and third sampling campaign mean level then divided by two. It was within the acceptable levels of the East Africa Standards (EAS) acceptable limits of 50 mg/L for natural portable water standards. The wet season had an average mean concentration of 130 mg/L which is approximately 160% higher than the acceptable limit by the East Africa Standards (EAS) acceptable limits for natural portable water. This might have been attributed by surface run-off as a result of rains introducing the suspended particles into the final discharge pond. Likewise, the high concentration of 840 mg/L recorded at Nairobi River at Outering was as a result of high rains hence surface runoff which carry solid particles with it and depositing them in the river system. Also, there was high organic wastes from both domestic and industrial wastes. Burst sewer liners also contributed to these high levels of pollution at this point. Pig farming and domestic animals grazing in this area contributed to pollution by animal wastes thus introducing solid particles into the river. Bridge construction and agricultural land use at this point was noticed to be one of the factors that contributed to river pollution by sediments.

TSS values often relate to the turbidity of water, that is, if TSS is high and the water is murky then it prevents light from the sun from penetrating well through the water. This makes plants and algae growth difficult therefore, reducing river productivity and generation of oxygen. Lots of sediments in water, for example, soil and silt can also clog fish gills and bury fish eggs when it settles to the bottom of a river bed (Data Stream, 2021)

5.1.2 Chemical parameters

5.1.2.1 pH

Nearly all river sample locations showed pH readings that were within the permitted ranges for naturally portable water set by the World Health Organization (WHO), East African Standards (EAS), and Kenya Bureau of Standards (KEBS) (5.5-9.5). The pH results from this investigation were in the range of 6.4 to 9.78. This confirmed the neutral characteristic of surface water as observed in rivers within the Athi river basin area. Beside any pollution factor, the high pH at the Athi River at Kibwezi station could be due to the photosynthetic activity of algae which was observed during sampling. According to Dirisu *et al*., (2016) pollution by effluents discharged into rivers may interfere with its pH. Comparatively Dulo, (2008) and Sila, (2019) reported pH 6.85-7.14 in Nairobi river and pH of 7.31±0.14 at Athi River, which are within the range of the results of this study and the natural pH of water is 7. In general, any pollutants that interact with a water supply of chemicals, minerals, soil or bedrock composition, among the many will cause an imbalance in the pH. For instance, if the carbonate, bicarbonate, or hydroxide chemicals are present in the soil or bedrock of the river, they dissolve and move with the water, changing the pH(Safe Drinking Water Foundation, 2017).

Aquatic creatures may experience stress as pH levels rise or fall, which will affect their ability to hatch and survive. Frogs, for instance, can tolerate a critical pH of approximately 4, but their prey, mayflies, cannot since they are more sensitive and may not survive pH below 5.5 (Wheeler, 2020). A species is more impacted by pH changes the more sensitive it is. Extreme pH values often enhance the solubility of elements and compounds, making hazardous substances more "mobile" and raising the danger of aquatic life absorption in addition to having biological impacts (Denchak, 2018). The slight acidic nature of most of these points with a pH range of between 6.4 – 6.98 was because of the contributes of organic matter decomposition within the water bodies releasing carbon (IV) oxide. The released carbon (IV) oxide combines with water forming weak carbonic acid thus dropping water pH, equation 9.

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \text{………………………….. (Equation 9)}$$

Then, one or both of the hydrogen ions in H_2CO_3 can be lost as illustrated in equation 10:

$$H_2CO_3 \Leftrightarrow HCO_3^- + H^+ \text{ …. } HCO_3^- \Leftrightarrow CO_3^{2-} + H^+ \text{…………. (Equation 10)}$$

Presence of certain metals in water, such as zinc, aluminium, and copper, as well as acidifying elements found in the bedrock beneath which the water is flowing. Oxides, sulphates, phosphates, nitrates, and carbonates, such as calcium oxide and sodium carbonates, are examples of these substances. Photoelectric reactions can also result in the creation of acidic oxides like SO_2 and NO_3, which readily dissolve in water and reduce the pH of the water (Wheeler, 2020).

The impacts of low pH in aquatic bodies include damage to gills from mucus development, stunted growth, ion control issues, reproductive failure resulting to a decrease in the number of species, and the replacement of acid sensitive species with acid resistant ones (Dirisu *et al*., 2016).

5.1.2.2 BOD and COD

The overall range of COD was 14 – 3360 mg/L. These results are in the same order of magnitude as those reported by K'oreje *et al*., (2016) (BOD 10-513 mg/L and COD 30 – 1278 mg/L) in the Nairobi sub-basin. High COD concentration of 1000 mg/L and 3360 mg/L with high mean concentrations of 330 mg/L and 560 mg/L were recorded in the first and third sampling campaign of the dry season.

These high values of COD in water indicated that there was a greater level of oxidizable organic matter. This was as a result of high evaporation resulting in high temperatures in the dry season. Consequently, lower levels of dissolved oxygen could eventually lead to eutrophication. This is true because COD is the quantity of oxygen required to completely oxidize all organic molecules, soluble and insoluble, present in a given volume of water (AOS, 2018). Therefore, eutrophication which is as a result of low dissolved oxygen levels, suffocates plants and animals, therefore it creates a dead zones where essentially water is devoid of life (Denchak, 2018)

However, BOD measurements ranged from 1 to 640 mg/L values which agreed with those reported by K'oreje *et al*., (2016) (BOD 10-513 mg/L). The highest value of 640 mg/L was recorded in Nairobi River at Outering Road in the third sampling campaign (dry season). The highest concentration of 600 mg/L and 640 mg/L were recorded in the dry season, that is, first and third sampling campaign, respectively. This may be due to various reasons which may include, microorganisms' presence, temperature, pH, type of inorganic and organic materials in the water. For example, the forementioned sampling points traverse the informal settlements of Kibera, Mathare and Ngomongo which experience high organic waste pollution. They were also sampled in the dry season in the afternoon when the sun was hot and overhead leading to high temperatures. These high temperatures and pH elevated the action of the microorganisms. As a result, microbes used more dissolved oxygen, directly affecting the amount of dissolved oxygen in surface water.

The rate of dissolved oxygen loss in the water body increases with increase in BOD value, meaning that higher aquatic life has less oxygen accessible to it. In addition to leaves and woody debris, food waste, dead plants and animals, wastewater treatment plant effluents, animal manure, feedlots, and food-processing facilities, failed septic systems, and urban stormwater runoff were further sources of organic matter wastes in these rivers. However, it is impossible to deny that the various kinds of pollution sources contributed to the rise in BOD and COD content. BOD was affected by these activities, such as the usage of agricultural land, urbanization, and industrialization, in both seasons.

High BOD has the same effects on aquatic life that low dissolved oxygen does, including stress, asphyxia, and death (Kanase *et al*., 2016). Dissolved oxygen levels might drop to dangerously low levels for aquatic life, such as fish. Through processes of reaeration of the river, which are caused by algae photosynthesis and air mixing, dissolved oxygen is replenished in surface water, gradually raising oxygen levels. Nitrates and phosphate fertilizers from the neighbouring agricultural fields into a water body through surface runoff can raise BOD levels by supplying plants and algae with nutrients for quick growth and microorganisms that decompose dead plants and discharge organic waste into the water cycle (Steven, 2017).

5.1.2.3 Sulphide

In the first, second, and third sampling campaigns, the mean concentrations were 5 mg/L, 16 mg/L, and 62 mg/L, respectively. Additionally, higher sulphide concentrations were found in the second and third sampling campaigns than in the first. This was due to the high existence of sulphate-reducing bacteria that anaerobically break down organic debris, effluents, dead algae, and the sulphur contained in fungicides, insecticides, and sulphur-based fertilizers than in the first sampling campaign. Sulphides also got entry into the water supplies from industrial waste as well as gasworks, paper mills, heavy water plants, tanneries, and petrochemical and petroleum facilities. Surface water sulphide was also as a result of the disposal of sulphate-based medications and supplements. This might be as a result of these medications or dietary supplements being directly disposed of into the aquatic habitat.

5.1.3 Nutrients

5.1.3.1 Orthophosphates

The high mean values of orthophosphates, that is, 10.79±3.13 mg/L and 5.03±4.63 mg/L were recorded in the first and second sampling campaigns, respectively. Comparatively, Chebet *et al*., (2020) reported phosphates concentration levels ranging from 0.13 mg/L – 11.06 mg/L in Molo River. These concentrations are lower than those reported in this study since Molo River experiences minimal effluent pollution as compared to the Athi basin.

Phosphate loading was the cause of the accumulation of orthophosphate in the surface water environment. Both naturally occurring orthophosphate and human activities might be to blame for this. These increase the amount of orthophosphate in surface water, which then recharges aquifers. Agricultural practices, particularly in the Athi basin's upper regions, are examples of human activity. For instance, one of the major factors is the extensive farming that takes place in Kikuyu and Kiambu counties. Manure, composted debris, and the use of artificial phosphorus fertilizers all add orthophosphate to these water supplies (Kent *et al*., 2020). These agricultural chemicals and fertilizers can find their way into water resources, for example, rivers by storm water runoff from agricultural fields and overflowing sewerage lines.

5.1.3.2 Ammonia and Nitrates

Ammonia is a biologically active compound and it is found in most waters as a result of normal biological degradation of proteins. It is also an indicator of the biochemical breakdown of organic nitrogen compounds. The third sampling campaign (dry season) recorded the highest value of 204 mg/L for ammonia with a mean value of 40 mg/L. On the other hand, highest value of 44 mg/L with a mean concentration of (20±12 mg/L) for nitrate (NO_3^-) was recorded in the second sampling (the wet season). The mean values of 15 mg/L, 26 mg/L and 40 mg/L were recorded in the first, second and third sampling campaigns, respectively. These mean values for ammonia were all high above the EAS, KEBS and NEMA ammonia permissible limits in raw water of 0.5 mg/L. However, Irungu, (2018) reported lower range of nitrates (0.4 mg/L -10 mg/L) and ammonia (0.1 mg/L – 2 mg/L) in river Sondu, which is attributed to low pollution input despite intensive agricultural activities around Sondu river. This may be due to the fact that only a tiny fraction of fertilizers applied may leak into ground and surface waters, but a big portion of them end up in the soil's organic nitrogen pool, where nitrogen is metabolized, taken up by plants, and/or lost by leaching over a long period of time (Bijay-Singh & Craswell, 2021).

The high ammonia content was caused by a high rate of nitrification, which is encouraged by the dry season's rising temperatures that are favourable to bacteria that fix nitrogen. Agricultural fertilizers discharge from agricultural lands near these rivers and surface runoff, both of which contain ammonia from industrial process wastes. Natural processes that include the breakdown or decomposition of organic waste material, such as human and animal waste results in nitrogen gas exchange with the atmosphere hence nitrogen fixation processes. Since ammonia gas has been utilized in municipal treatment systems for more than 70 years to extend the efficiency of disinfection of chlorine added to drinking water, waste water treatment facilities may also be a factor in this. This increases the production of chloramines, which might provide unpleasant tastes, while decreasing the production of chlorination by-products, which could be carcinogenic (USEPA, 2013b; Water Quality Association, 2013).

The mean values of 8 mg/L, 20 mg/L and 0.61 mg/L recorded in corresponding first, second and third sampling campaigns were below the EAS allowable limit of 45 mg/L for natural portable water. High mean levels of nitrates of 20 mg/L in the second sampling campaign (wet season) were as a result of increased water volume in these water resources due to the high rainfall. Therefore, this resulted in surface runoff water which entered into these rivers passing through agricultural fields. Soil particles that are enriched with both organic manure and inorganic fertilisers carried with it into these water resources. Another contributor is a consequence of immense land cultivation around surface water bodies involving excessive use of inorganic nitrogen-based fertilizers, manures, wastewater treatment, and the oxidation of nitrogenous waste products in human and animal excrement in agricultural farming (for example, septic tanks). Nitrogen based fertilizers containing inorganic nitrogen and wastes containing organic nitrogen are first decomposed to give ammonia, which is then oxidized to nitrite and nitrate (WHO, 2011b).

Meanwhile the third sampling campaign registered the lowest mean concentration than the first sampling campaign despite the fact that they were both sampled in the dry season. This might have been contributed by the high rate of denitrification process and high plants uptake of the nitrate nutrient in the third sampling campaign with most rivers recording ND nitrate concentrations as compared to the first sampling campaign (Nyilitya *et al*., 2020).

Kariobangi WWTP recorded ammonia concentration in the range of between 37 - 204 mg/L and nitrates level in the range of ND – 26 mg/L. The highest values of 204 mg/L were above the KEBS and NEMA tolerable limits of 100 mg/L for ammonia and nitrates in treated effluent discharge into a natural water source. However, nitrates were within the tolerable limits by KEBS and NEMA. Ammonia and nitrates levels reported at Ruai WWTP were within the tolerable levels for discharge into public water by KEBS and NEMA. This indicated that the stabilization ponds method employed by Ruai WWTP seems to be an effective method for removal of ammonia and nitrates in wastewater as opposed to the trickle method employed by Kariobangi WWTP (Salmani et al., 2014). This is evident in the results of the two nutrients recorded with low values at Ruai WWTP while high levels at Kariobangi WWTP were recorded in the dry season. Therefore, Kariobangi WWTP is identified as a point source of nutrient pollution to the Nairobi River into which it discharges its treated effluents.

Due to denitrification processes, the extremely low nitrate values of ND (no-detection) found in the aforementioned areas of the watershed may be caused by nitrate removal processes (Nyilitya *et al*., 2020). Surface water contains ammonia because nitrification is being impeded (the oxidation of ammonia to nitrite [NO_2^-] and nitrate [NO_3^-]).

High nutrients affect these surface water ecosystems by accelerating their aging process for example, lakes. Additionally, it increases the overproduction in water bodies, which causes an imbalance in the process of nutrition and material cycle. Eutrophication ("well fed") increases primary producer output, which lowers ecological stability. Over the last several decades, it has become clear that excessive nutrient inputs, typically nitrogen and phosphate-based fertilizers, are the primary source of eutrophication. This aging process may cause significant changes in the trophic status and quality of the surface water, as well as in some situations, cyclical cyanobacterial blooms (Know your water, 2020). Moreover, the biota in benthic or surface water may be poisoned by ammonia produced in surface water in general (Lapota *et al*., 2000; USEPA, 2022).

5.2 Seasonal variation of physical-chemical parameters

Generally, there was no significant difference between the concentration distribution of the first and the second sampling campaigns. This is clearly seen from the look of their close median concentration of 25 mg/L and 27 mg/L, respectively. Mean values distribution of these two (first and second) samplings campaign of 111 mg/L and 122 mg/L also illustrates this. However, the third sampling campaign recorded the highest concentration distribution of these physical-chemical parameters. This is because a mean value of 177 mg/L and a median value of 41 mg/L were recorded. This minimal concentration variation between the first and second sampling campaigns is attributed to seasonal changes.

The third sampling campaign recorded high concentration distribution range as a result of high temperatures arising from scorching sunshine during the dry season. This relatively increased the overall temperature of the river which in turn led to high levels of water evaporation in rivers within the Athi river basin. Since high temperature influences the overall reactivity of some chemically and physiological reactions in water, it influences increase in concertation of these parameters in the dry season. For example, the highest recorded concentration of 3360 mg/L was for COD, ammonia of 204 mg/L, sulphide of 192 mg/L, TDS of 1243 mg/L and BOD of 640 mg/L as compared to the first and second sampling campaigns. These water quality parameters are really temperature dependent. This actually confirms the effect of seasonal changes on the concentration of physical-chemical parameters, that is, the increase in temperature increases chemical reactions which in turn increases the concentration of some chemical-based and physiological parameters.

However, during the second sampling campaign (wet season) the levels of these parameters were subsequently low as compared to those of the third sampling campaign. This is because of increased water volume in these rivers within the Athi River basin area thus diluting the concentration of the parameters thus the low values. Increased rainfall and surface runoff relatively added more water into the rivers thus slightly increased the overall concentration of these parameters as compared to first sampling campaign (dry season). This is evident in TDS with a value of 1085 mg/L recorded in the first sampling campaign (dry season). The TDS slightly increased in the second sampling campaign (wet season) to 1203 mg/L. This increase in amount of TDS is as an attribute of rainfall and surface runoff which in turn dissolved other soluble solids and introduced them into the river water. This is especially more evident in regions where there was runoff through agricultural lands with immense use of inorganic fertilizers. The rainfall also reduced the surrounding temperature which in turn also lowered the reactivity of some chemical components in the water and also the activity of temperature depended microorganisms (Mohammad *et al*., 2017).

5.3 Bacteriological Studies

Bacteria were recorded in the range of 1 - 1.79×10^7 cfu/100 mL, with total coliforms recording the highest concentration counts in the range of 20 - 5.885×10^7 cfu/100 mL. *E. coli* followed closely in the range of 4 - 1.79×10^7 cfu/100 mL. Salmonella and shigella both recorded a narrow distribution range between them with a range of 1 - 1.01×10^2 counts/100 mL and 1 – 1.11×10^2 counts/100 mL, respectively. These bacterial counts were high above the EAS, KEBS and NEMA threshold levels of NIL/100 mL for natural portable water for all the four bacterial genuses analyzed. Wambugu *et al*., (2015) also reported a high average coliform counts of 2.7×10^4 cfu/mL in Athi river. Musyoki *et al*., (2013) also reported low salmonella paratyphi (1.6×10^1 counts/100 mL), salmonella typhi (2.1×10^2 counts/100 mL) and shigella flexneri (1.2×10^1 counts/100 mL) level as compared to coliforms bacteria. *E. coli* bacteria is a subgroup of faecal coliforms which in turn is a sub-group of total coliform bacteria which show the relationship between these two pollution indicators (Francy *et al*., 1993). Warm-blooded animals' and humans' intestines contain large numbers of the innocuous *E. coli* bacterium. Its presence in water is a sign of faecal contamination. Wastewater treatment facilities, failing septic systems (such as sewage overflows from clogged or pierced sewer lines that drain into the rivers), household and wild animal faeces, and malfunctioning septic systems are all potential causes of faecal pollution. Additionally, owing to open defecation, stormwater runoff introduces faecal wastes into the water system. Additionally, pit latrines built in riparian locations, where they primarily discharge into rivers.

Upstream Rivers recorded relatively high bacterial counts since they are located within the formal settlement setup. Rivers at this stage experiences relatively minimal pollution levels as compared to those traversing through the informal settlement where poor sanitation is highly experienced. Mbagathi River at Ngong road recorded bacterial counts of 3 – 7.77×10^2 counts/100 mL. The bacterial count here was a bit high for an upstream river. There was subsistence farming which might be the cause of bacterial activities due to application of organic fertilizers. Also, there were animal watering points in the river resulting to pollution by animal wastes. Open defecation also contributed to pollution. Mbagathi River at Rongai recorded bacterial counts of 10 – 1.203×10^3 counts/100 mL. This was relatively high but at this sampling point, there was a direct discharge of raw domestic wastewater into the river system therefore introducing organic matter which elevated the bacterial count. Ngong River at Ngong forest recorded the second lowest bacterial count of 6 – 1.34×10^3 counts/100 mL with total coliform recording the highest of 1.34×10^3 bacterial counts/100 mL. Despite the fact that the river traverses through the Ngong forest the population from the Kibera slums could still access it for bathing and laundry purpose and hence practiced open defecation on its banks. Nairobi river at Kikuyu recorded the least bacterial count of 2 – 23 counts/100 mL with shigella recording the highest of 23 counts/100 mL while salmonella the lowest of 2 counts/100 mL this is because the river at sampled point traverses' agricultural land.

Salmonella and shigella had the lowest numbers of total coliforms and *E. coli* bacterial genera in the middle stream at this time. These rivers traverse informal settlements such as

Kibera, Mathare, Ngomongo and industrial area. These informal settlements have poor sanitary infrastructure, therefore domestic wastewater is directly released into the river and open defecation is highly practiced here. Moreover, pit latrines are constructed in the riparian areas from where they mainly empty into the rivers. Additionally, sewer overflows from blocked or punctured sewer lines often drain into the rivers in these areas. These areas contribute to an increased organic waste pollution indicating presence of more bacteria decomposing these wastes using dissolved oxygen. However, rivers that traverse the formal settlements recorded low bacterial counts as compared to those traversing the informal settlements. For example, Nairobi River at Museum hill 33 – 7.03×10^5 counts/100 mL, Athi River at Kangundo Road 1 – 2.4×10^5 counts/100 mL, Ngong River at Kangundo Road 6 – 1.104×10^4 counts/100 mL confirm minimal organic matter pollution in these areas.

Downstream rivers recorded low bacterial counts varying from 0 counts/100 mL to 3.4×10^5 counts/100 mL as compared to the midstream rivers which recorded counts varying from 0 counts to 1.9×10^7 counts/100 mL. This is because at such points rivers receive treated wastewater discharged into them by the WWTP join the basin. For example, Nairobi River just after confluence with Ngong River receive discharged treated wastewater from Ruai WWTP. Also, rivers that traverse informal settlements such as Ngong River at Kibera, Mathare River and Nairobi River at Ngomongo joins the basin immediately. For example, Ngong River at Kibera is a site that is situated at the heart of the Kibera informal settlement. These informal settlements have poor sanitary infrastructure, thus domestic wastewater is directly discharged into the rivers.

Athi river at Wamunyu recorded the second highest bacterial counts of between 0 - 1.44×10^5 counts/100 mL followed by Athi river at Kibwezi and Little Kiboko river. The bacterial counts considerably reduce downstream from Nairobi River at Juja farm to Athi river at Kibwezi which recorded bacterial counts of between 1 – 5.6×10^{1} counts/100 mL. This is as a result of great reduction in organic matter pollution which is contributed by proper sanitary infrastructure. Thus, there is generally minimal or complete lack of domestic wastewater directly discharged into the rivers. Also, bacteria from other areas might have died on the way or been consumed by other bacterial predator organisms such as fish therefore, reducing their population. On the other hand, the Little Kiboko river which is as a result of spring aquifer (groundwater source) recorded low bacterial count of between 0 – 1.21×10^{2} counts/100 mL because this river flows through restricted area and therefore experiencing minimal human interferences.

Kariobangi WWTP which employs trickling filter technology and discharges its effluent into Nairobi River before confluence with Mathare river recorded the highest bacteriological concentrations of 6 – 1.2×10^{7} counts/100 mL with total coliforms (1.2×10^{7} cfu/100 mL) and *E. coli* (8.35×10^{6} cfu/100 mL) compared to salmonella (25 counts) and shigella (6 counts/100 mL). However, Ruai WWTP which employs wastewater stabilization pond technology discharges its effluent into Nairobi River just after confluence with Ngong River recorded considerably low bacterial counts of 4 – 1.01×10^{2} counts/100 mL. Salmonella (1.01×10^{2} counts/100 mL) and total coliforms (35 cfu/100 mL) were the highest while shigella (6 counts/100 mL) and *E. coli* (4 cfu/100 mL) were lowest recorded counts. This indicates that stabilization pond technology employed by Ruai WWTP is the best technology for bacteriological control in wastewater treatment. Consequently, the trickling filter technology employed by Kariobangi WWTP which uses bacteria for wastewater treatment increased the number of bacteria in the wastewater treated (Salmani et al., 2014). This consequently, introduced these bacteria into water resources into which they are discharged.

5.4 Heavy Metals Studies

5.4.1 Distribution of Heavy metals in rivers within Athi river Basin area

Mid-stream rivers recorded the highest heavy metals concentration especially in Mathare River at Gomongo, Mathare River at Outering Road, Ngong River at Kangundo Road, Ngong River at Outering, Nairobi River at Museum Hill, Ngong River at Kibera Lindi bridge and Mathare River at Thika Road. These rivers traverse the informal settlement where there was high raw domestic wastes pollution. These raw wastes contained supplements-based foods and drugs that can lead to pollution from these metals. Also, there was lack of proper sanitary facilities like toilets leading to open defecation and poor drainage system whereby all wastes were drained into the river system. Heavy metals have been found to enter aquatic resources through the discharge of industrial, municipal, and agricultural wastewaters and sewage into rivers. For instance, Shamuyarira & Gumbo, (2014) observed that samples of sewerage sludge taken from five different places around the Limpopo region of South Africa contained high levels of Cd, Pb, Zn, and Cu that were beyond the recommended guidelines (Agoro *et al*., 2020). Rivers at Outering recorded highest heavy metals levels since they traverse through the industrial area despite the fact that they also traverse through the informal settlements. These industries might dispose of containers containing heavy metals-based chemicals which may in turn be introduced into the river via surface runoff. Also, burst and overflowing sewers especially in these areas drained their wastes into Nairobi River at Outering this could have elevated the concentration levels in its waters. Nairobi River at Museum Hill also traverse near a motor vehicle mechanic garage yard which might be a contributing factor of heavy metals in water. This is because of open disposal of the dry cell car batteries and car metallic parts which are brought into the river through surface runoff.

Wastewater treatment plants recorded same concentration range as those of upstream rivers. This indicates that the treatment methods applied by these two wastewater treatment plants are somewhat effective.

5.4.2 Heavy metals concentration in Athi river basin area

Metals were recorded in the range varying from ND to 7.6 ppm, **Table 4.4**. Chromium, Cr, cadmium, Cd and copper, Cu, were not detected while iron, Fe, recorded in the range of 0.01 ppm to 7.6 ppm, manganese, Mn, was recorded in the range ND to 4.3 ppm, lead, Pb, in the range of ND – 0.7 ppm and zinc, Zn, in the range of ND – 3.4 ppm.

5.4.2.1 Copper, Cadmium and Chromium

These three metals were not detected (ND) in all the sampling campaigns. This indicated either they were absent in the water or their levels were below the detection limit. Similarly, Gaiti *et al*., (2018) also reported not detected (ND) concentrations for these metals in Ngong Tributary of Nairobi River which was in line with the results of this study. These recorded concentrations were in line with the EAS maximum allowable limits of 1.0 mg/L, 0.003 mg/L and 0.05 mg/L in natural portable water for copper, cadmium and Chromium, respectively.

5.4.2.2 Lead

Lead levels were found to range from ND to 0.7 mg/L. Similarly, Kakoi *et al*. (2015) recorded mean lead concentrations of 0.5-0.6 mg/L in Gitathuru River, 0.6 mg/L in Nairobi

River, and 0.6 mg/L in Ngong River surface water. These levels matched with those noted throughout this investigation. Lead levels were much higher in the first and third sample campaigns (dry season) than in the second sampling campaign (wet season). The lowest values, which ranged between ND and 0.02 mg/L, were reported during the second sampling phase. The Ruai WWTP recorded the highest value of 0.02 mg/L whereas Kariobangi WWTP recorded the lowest concentration of 0.0001 mg/L among the WWTPs. Lead levels in Ruai WWTP recorded above the 0.1 mg/L KEBS acceptable limits for discharge into sources of surface water. This suggests that Kariobangi WWTP's trickling treatment approach was far more successful than Ruai WWTP's usage of waste stabilization ponds.

All of the rivers in the Athi basin had the lowest levels of ND, though. Heavy rains and surface runoff caused the rivers water volume to expand, diluting the metal content and contributing to the ND in these rivers. Nairobi River had the lowest concentration of ND, whereas the third sample campaign had the greatest concentration in the range of ND - 0.7 mg/L. Given that this river is an upstream river and does not pass through any informal or official settlements, explains why there was minimal or no human contamination in the region. Ruai WWTP, on the other hand, recorded the highest value of 0.7 mg/L. The industrial waste that is brought into the facility for treatment could be the contributor to this high percentage.

Industrial wastes could be one of the potential sources of lead in the treated wastewater (for example, used lead acid batteries, solder, alloys, cable sheathing, pigments, rust inhibitors and plastic stabilizers). Thus, wastewater treatment facilities might be a single point source of lead pollution in the rivers of the Athi river basin. High levels of lead, in the body causes harm to the brain and central nervous system and induce headaches, anemia, and colic (Rehman *et al*., 2013).

5.4.2.3 Iron

With concentrations ranging from 0.02 to 7.6 mg/L, iron was the highest recorded heavy metal in the Athi river basin for this study. In comparison, Njuguna *et al*. (2017) stated that iron content in Nairobi River ranged from 0 to 11.9 mg/L, and the results of this study are within this range. Little Kiboko river had the lowest value, which was 0.02 mg/L. The highest threshold levels for natural portable water were 0.3 mg/L, which fall below EAS and KEBS. Since this river had an underground water source and was less polluted by human activity, it was the consequence of natural processes in the bedrock underneath. However, Mathare River at Ngomongo, where the greatest quantity of 7.6 mg/L was found experiences, severe anthropogenic contamination caused by raw home waste spills and raw sewage wastes from sewer pipes that have burst or blocked. Additionally, supplement-based meals and pharmaceuticals that were improperly disposed of were introduced into rivers by surface runoff could also contaminate the water.

5.4.2.4 Manganese

The second-highest metal found in the Athi river basin was iron, which was found at concentrations between ND and 4.3 mg/L. These findings, however, are in the same order of magnitude as those found in the Nairobi River by Kakoi *et al*. (2015), who found values of (5 mg/L and 6 mg/L) during dry weather and (1 mg/L and 3 mg/L) during rainy season. For the range between 0.001 and 4.3 mg/L, the maximum concentration was found during the second sampling cycle. The Nairobi River in Kikuyu had the lowest value, which was 0.001 mg/L, within the 0.1 mg/L EAS and KEBS permissible levels. The greatest quantity was 4.3 mg/L in the Mbagathi River in Rongai, which was above the EAS and KEBS allowable limits of 0.1 mg/L. This value was the highest recorded in this river in the three sampling campaigns. This showed an increase in the manganese concentration as compared to the concentrations registered in the first and third sampling campaigns.

This was as a result of surface runoff attributing to the increase by introducing manganese containing wastes from manganese-based chemicals, food supplements and drugs. Also, Rongai is an upcoming urban centre with poor sanitation and drainage facilities. Therefore, this river received highly polluted raw domestic wastes through direct discharge from the surrounding residential apartments. Also, burst and blocked sewer line leaked their contents into the river. Interestingly the first and third sampling campaigns recorded the same concentration ranges varying from ND mg/L to 3.1 mg/L. Ngong river at Ngong forest and Little Kiboko recording the lowest value of ND while Ngong River at Kibera and at Kangundo Road recorded the highest concentration of 3.1 mg/L. This value was high above the KEBS allowable limits of manganese of 0.1 mg/L for domestic water. It could have been contributed by heavy pollution from domestic wastes which contains manganese-based chemicals.

Ngong river traverses the informal settlement of Kibera which experiences heavy pollution through raw domestic wastes. It also traverses the industrial area and industries located along this Ngong River tributary could be contributing significant amounts of manganese.

5.4.2.5 Zinc

Zinc content ranged from ND to 3.4 mg/L. Comparatively, Muiruri *et al*. (2013) reported zinc levels in Athi-Galana-Sabaki tributaries varied between 0.046 and 0.695 mg/L and 0.010 and 0.055 mg/L throughout the wet and dry seasons, respectively. These results were within the range of results reported in this present study. This concentration range was within the 5 mg/L of KEBS and EAS permissible limits of zinc in natural portable water. The first and second sampling campaigns recorded concentrations ranging from ND – 3.4 mg/L and 0.01 mg/L to 3.4 mg/L. That is, both these sampling campaigns recorded same highest level of 3.4 mg/L in Ngong River at Kibera and Ruiru River respectively.

The high level in Ngong River at Kibera was due to high pollution by domestic wastes which contributed to contamination by zinc-based food and drugs. On the other hand, Ruiru river experienced pollution from steel-based industries in the surrounding areas. For example, an overflowing sewer line from one steel-based industry was spotted draining into the Ruiru river. This elevates the zinc level in Ruiru River. The low concentrations of ND and 0.01 mg/L were recorded in Thiririka River and Nairobi River at Kikuyu. These values were within the KEBS maximum allowable limits for zinc of 1.5 mg/L. The low levels were within tolerable limits and could have been as a result of these rivers being an upstream river thereby experiencing minimal to no contamination by zinc-based pollutants.

Conversely, the third sampling campaign registered zinc levels in the range of ND – 2.1 mg/L. These were recorded in Nairobi River at Kikuyu and Ruirwaka River. Nairobi River at Kikuyu is an upstream River hence experiences minimal or no zinc pollution. Meanwhile, Ruirwaka River traverses the upcoming urban settlement of Rwaraka and Lucky summer which contribute to raw domestic wastes pollution. Also, spillage sewer line passing over the river and presence of a slaughter house in the vicinity might be the main contributors to this high zinc concentration (Ukpong, 2012).

5.4.3 Seasonal Variation of heavy metals

The first sample campaign had the largest dispersion of heavy metals, with readings between ND and 7.6 mg/L, followed by readings between ND and 7.5 mg/L and readings between ND and 4.04 mg/L. This seasonal variance was distributed considerably differently between the first sampling campaign (dry season) and the second sampling campaign (wet season). The considerable rainfall during the wet season, which diluted the concentration of these metals, was linked to this. However, the third sample session (dry season) showed the lowest dispersion because of substantial evaporation at this time of year because of the high temperatures. Due to adsorption on the surface of the floating particulate matter, there could have been a low concentration of these heavy metals as a result (Zhang *et al*., 2010). These left high concentration of sediments and suspended solids as clearly illustrated by TSS in the third sampling campaign which had values higher than the first sampling campaign. Due to adsorption on the surface of these floating particles, there could have been a low concentration of these heavy metals as a result (Herngren *et al*., 2005; Nasrabadi *et al*., 2018).

CHAPTER SIX

CONCLUSION AND RECOMENDATIONS

6.1 Conclusion

The entry of raw effluent, could have contributed to high values of BOD and COD, into the water systems. Poor agriculture practices near these surface water sources also polluted rivers with nutrients by introducing both organic and inorganic fertilizers.

Open defecation, poor sanitation in informal settlements (such as Kibera, Mathare, and Gomongo), raw residential and industrial effluent pollution, and organic matter pollution in the river systems all contributed to high levels of bacterial contamination, including *E. coli* and total coliforms. Mathare River at Outering Road had the highest count, followed by the Mathare River at Ngomongo, and Mathare River at Thika Road.

The primary causes of heavy metals pollution were shown to be industrial wastes, dumping grounds, raw domestic wastes containing supplements-based foods and medication wastes, and wastewater treatment facilities. These metals were in higher amounts in the following sequence of declining concentration: Fe > Mn > Zn > Pb > Cd, Cr, and Cu. Iron and zinc in these rivers were mostly caused by industrial wastes from steel and iron sheet-based companies, particularly in the Ruiru region. Additionally, Lead contamination in these rivers may have been as a result of improper disposal of dry cells and acid lead accumulator batteries. On the other hand, metal-based medications and supplements dumped in landfills like the Dandora dumping site may have led to elevated levels of iron, zinc, and manganese pollution.

Finally, it was discovered that the majority of the water quality measures examined exceeded EAS threshold limits.

6.2 Recommendations

Before being released into surface water bodies, wastewater effluents must be properly treated using efficient wastewater treatment techniques. The consumers of surface water resources will experience less of a health risk as a result. Farmers should adapt practices such as organic farming and integrated pest management which could help in protecting surface water sources. They should also minimize or avoid the use of chemicals for industrial, agricultural, and domestic purposes. This is an ideal method to abate diffuse chemical pollution into our waterways.

In informal settlements (such as Kibera, Mathare, and Gomongo), proper sanitary facilities should be offered. This would lessen the problem of open defecation along river banks and forests, which ends up in surface water due to runoff during the rainy seasons polluting water bodies. This will in turn aid in the control of bacterial contamination, including *E. coli* and total coliforms.

Heavy metal contamination is brought on by places where waste is dumped, such as the Dandora dump site and wastewater treatment facilities, as well as raw domestic wastes containing food supplements and medicine wastes. For instance, incorrect disposal of dry cells and acid lead accumulator batteries results in lead contamination. Therefore, law enforcement organizations should enhance the regulations controlling the disposal of heavy metals wastes. This should lead to longer sentences and tougher maximum penalties. As violations become more serious, higher management is held accountable rather than local staff.

6.3 Suggestion for future studies

In order to address the pollution issue in the Athi river basin area, more research is required on other harmful heavy metals as mercury, arsenic, cobalt.

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APPENDICES

Appendix I: EAS physical-chemical, heavy metals and bacteriological parameters requirements for natural portable water.

System parameter	unit	Guideline value
pH		5.5 – 9.5
Electrical conductivity	µs/cm	2500
Ammonia	mg/L	0.5
Nitrates	mg/L	45
TDS	mg/L	1500
TSS	mg/L	Nil
Copper	mg/L	1.0
Cadmium	mg/L	0.003
Chromium	mg/L	0.05
Iron	mg/L	0.3
Lead	mg/L	0.01
Zinc	mg/L	5
Manganese	mg/L	0.1
Total coliforms	cfu/100 mL	Nil
E. coli	cfu/100 mL	Nil
Shigella	counts/100 mL	Nil
Salmonella	counts/100 mL	Nil

Appendix II: WASREB physical-chemical, heavy metals and bacteriological parameters requirements for drinking portable water.

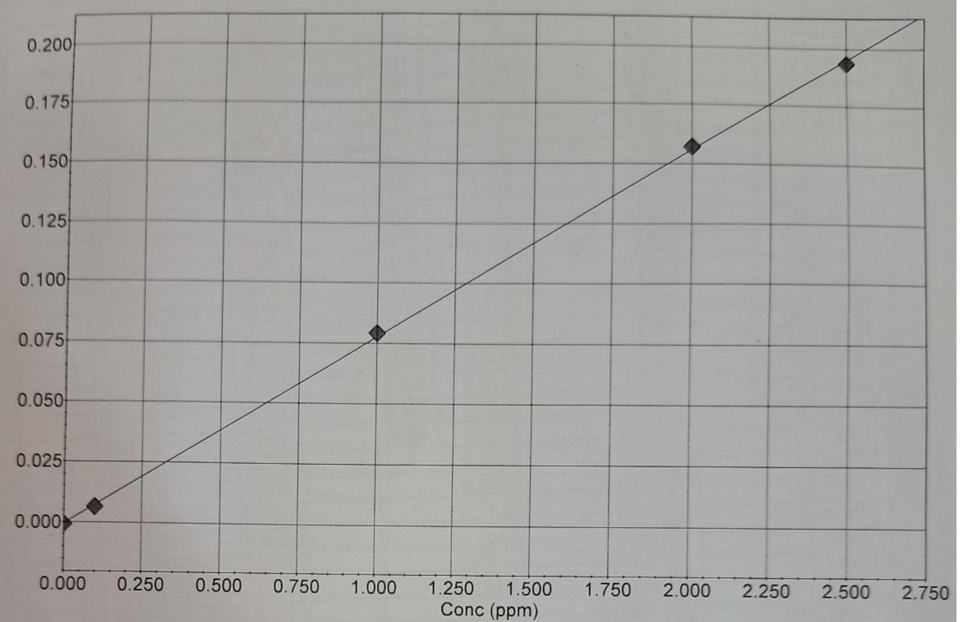
System parameter	unit	Guideline value
pH		6.5 – 8.5
Electrical conductivity	µs/cm	2500
Ammonia	mg/L	0.5
Nitrates	mg/L	10
TDS	mg/L	1200
TSS	mg/L	Nil
Copper	mg/L	0.05
Cadmium	mg/L	0.01
Chromium	mg/L	0.05
Iron	mg/L	0.3
Lead	mg/L	0.05
Zinc	mg/L	5
Manganese	mg/L	0.1
Total coliforms	cfu/100 mL	Nil
E. coli	cfu/100 mL	Nil
Shigella	counts/100 mL	Nil
Salmonella	counts/100 mL	Nil

Appendix III: WASREB and NEMA physical-chemical, heavy metals and bacteriological parameters requirements for discharge into public water.

System parameter	unit	Guideline value
pH		6.5 – 8.5
Electrical conductivity	µs/cm	2500
Ammonia	mg/L	100
Nitrates	mg/L	100
TDS	mg/L	1200
TSS	mg/L	30
Copper	mg/L	1.0
Cadmium	mg/L	0.01
Chromium	mg/L	2.0
Iron	mg/L	10.0
Lead	mg/L	0.01
Zinc	mg/L	0.5
Manganese	mg/L	10.0
Total coliforms	cfu/100 mL	30
E. coli	cfu/100 mL	Nil
BOD (5 days at 20 ℃) max	mgO_2/L	30
COD, max	mgO_2/L	50
Temperature	℃	±3 of ambient water body temperature
Sulphides	mg/L	0.1

Appendix IV: Iron, Fe, AAS calibration curve

Calibration Curve(Element:Fe:FlameCont C#:01)

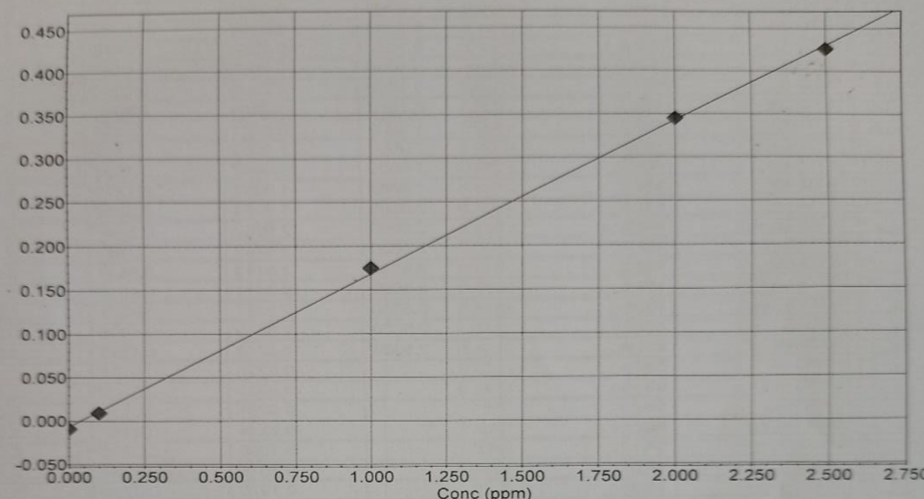


Abs=0.078244Conc-0.00053304 r=0.9999

CONC	ABS
0.0000	-0.0008
0.1000	0.0064
1.0000	0.0792
2.0000	0.1571
2.5000	0.1936

Appendix V: Manganese, Mn, AAS calibration curve

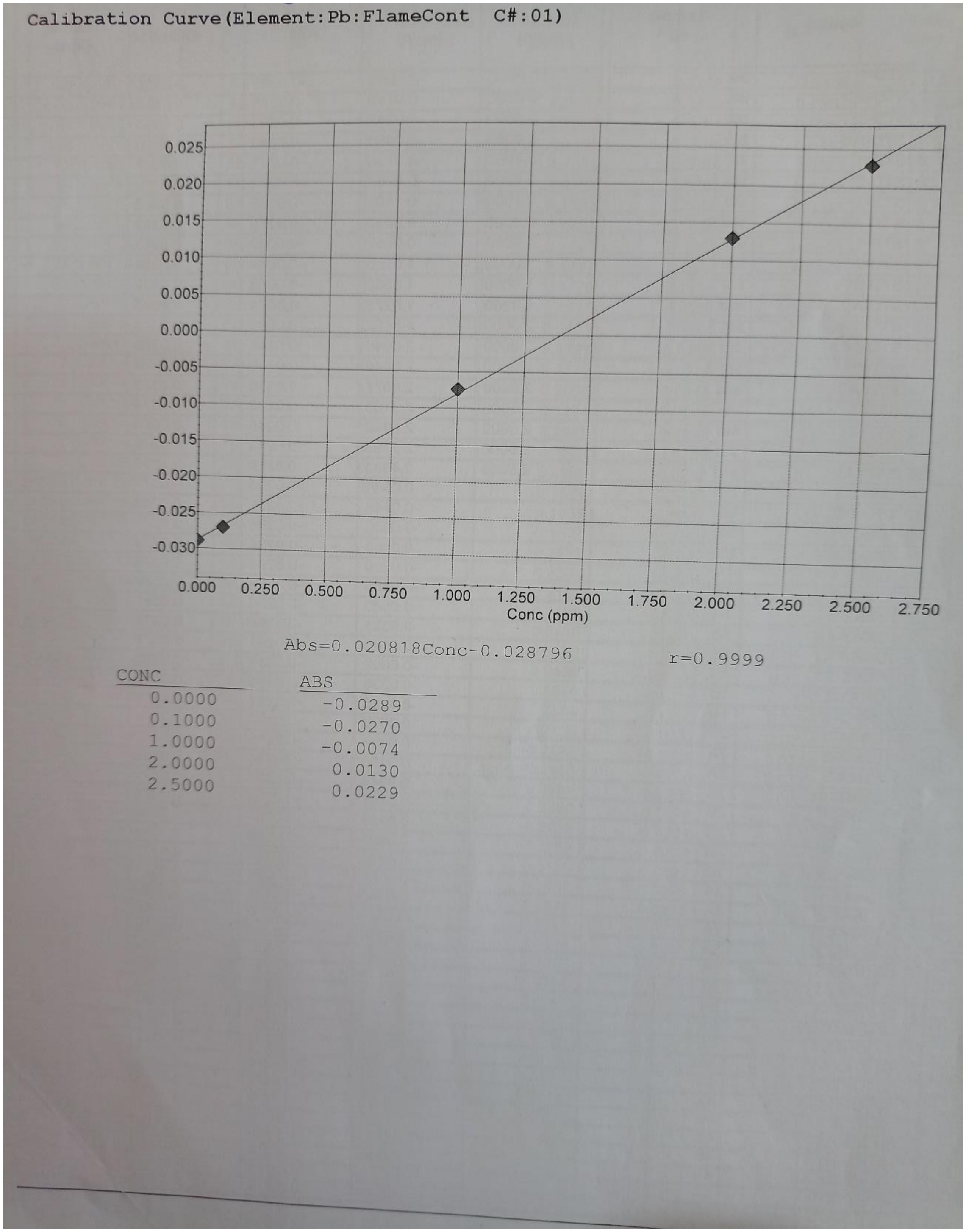
Calibration Curve(Element:Mn:FlameCont C#:01)



Abs=0.17478Conc-0.0064303 r=0.9997

CONC	ABS
0.0000	-0.0092
0.1000	0.0093
1.0000	0.1751
2.0000	0.3451
2.5000	0.4263

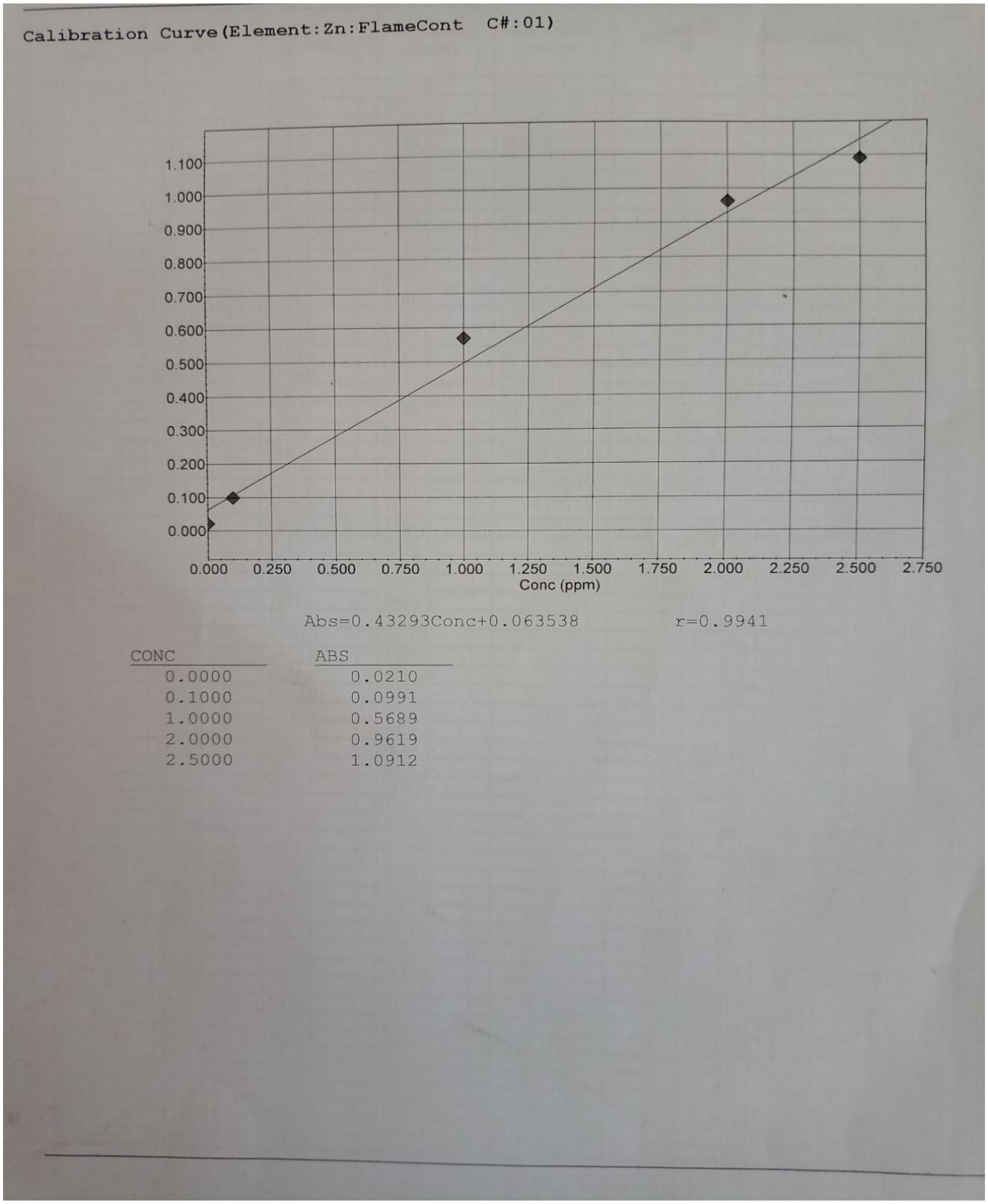
Appendix VI: Lead, Pb, AAS calibration curve



Abs=0.020818Conc-0.028796 r=0.9999

CONC	ABS
0.0000	-0.0289
0.1000	-0.0270
1.0000	-0.0074
2.0000	0.0130
2.5000	0.0229

Appendix VII: Zinc, Zn, AAS calibration curve



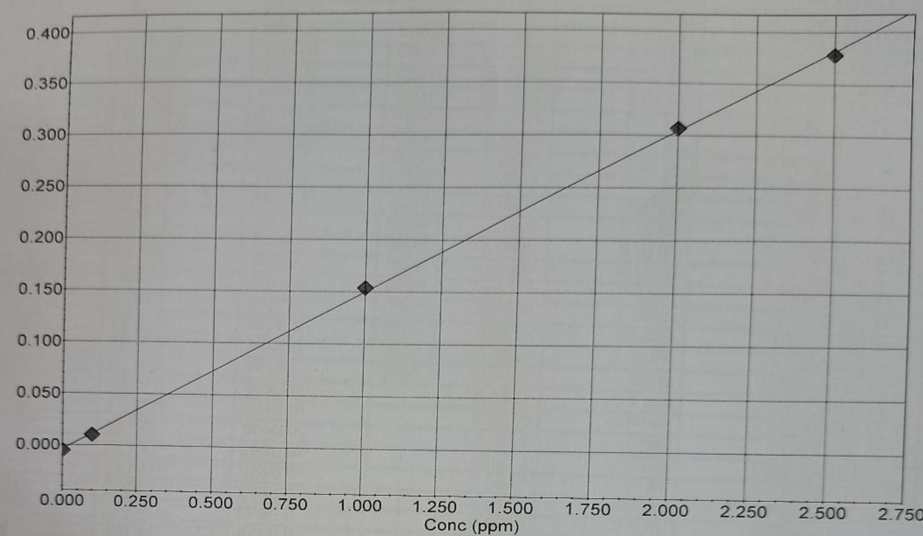
Calibration Curve(Element:Zn:FlameCont C#:01)

Abs=0.43293Conc+0.063538 r=0.9941

CONC	ABS
0.0000	0.0210
0.1000	0.0991
1.0000	0.5689
2.0000	0.9619
2.5000	1.0912

Appendix VIII: Copper, Cu, AAS calibration curve

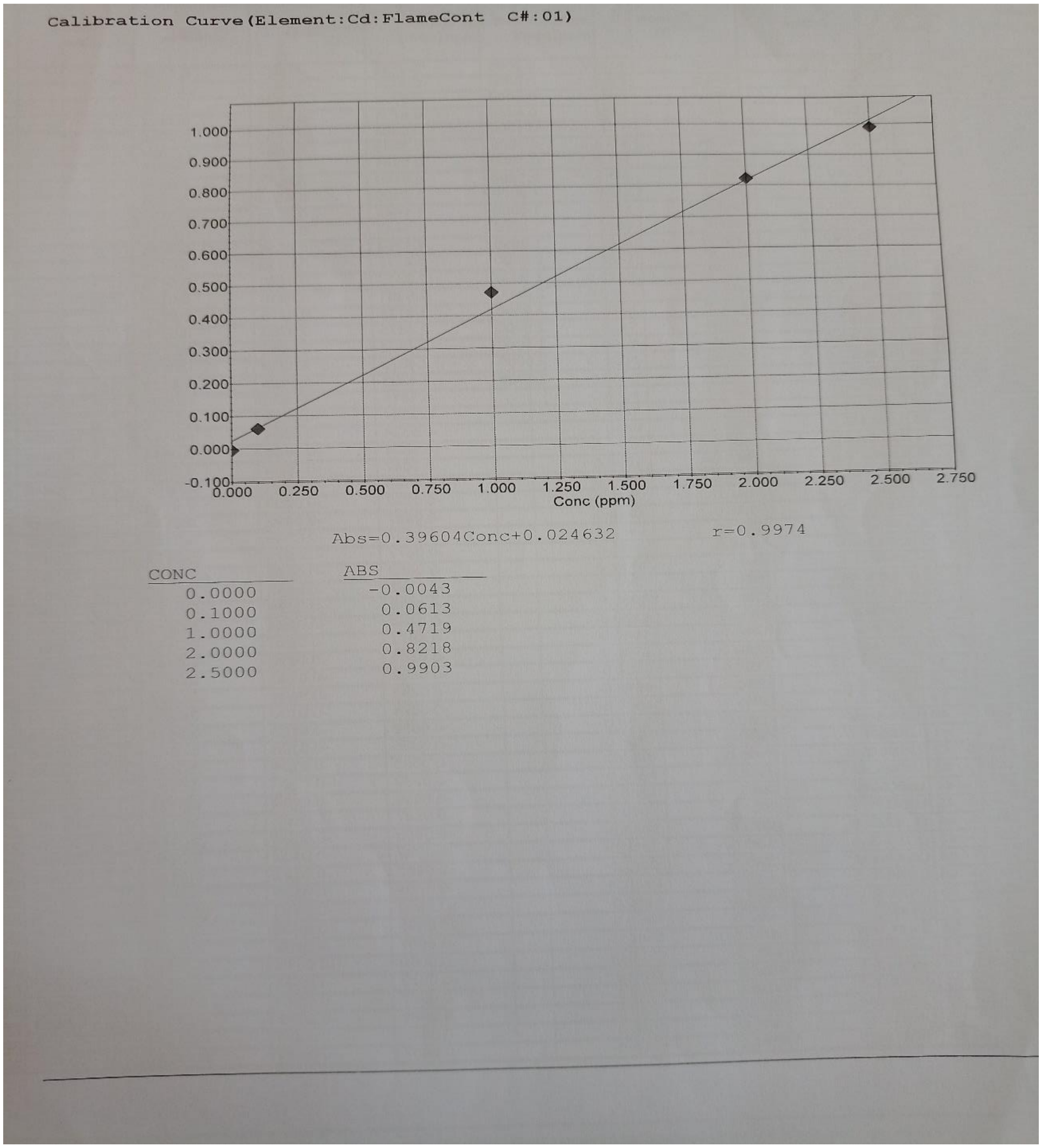
Calibration Curve(Element:Cu:FlameCont C#:01)



Abs=0.15431Conc-0.0041231 r=0.9999

CONC	ABS
0.0000	-0.0055
0.1000	0.0100
1.0000	0.1538
2.0000	0.3068
2.5000	0.3784

Appendix IX: Cadmium, Cd, AAS calibration curve

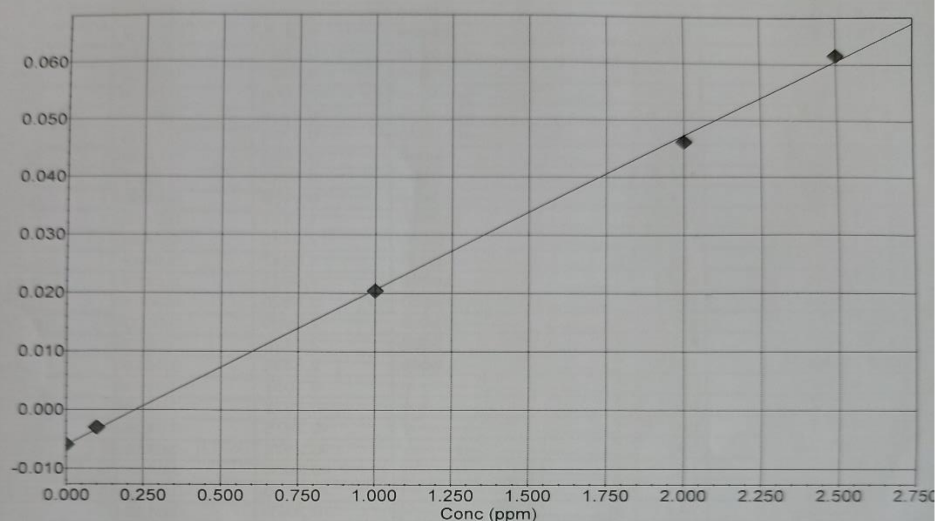


Abs=0.39604Conc+0.024632 r=0.9974

CONC	ABS
0.0000	-0.0043
0.1000	0.0613
1.0000	0.4719
2.0000	0.8218
2.5000	0.9903

Appendix X: Chromium, Cr, AAS calibration curve

Calibration Curve(Element:Cr:FlameCont C#:01)



Abs=0.026623Conc-0.0059779 r=0.9996

CONC	ABS
0.0000	-0.0059
0.1000	-0.0030
1.0000	0.0204
2.0000	0.0461
2.5000	0.0616

Appendix XI: Turnitin report

Turnitin Originality Report

WATER QUALITY OF ATHI RIVER AND ITS TRIBUTARIES BASED ON SELECTED PHYSICAL-CHEMICAL PARAMETERS, HEAVY METALS AND BACTERIAL LEVELS by Philip Sewe

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