



UNIVERSITY OF NAIROBI

**ASSESSMENT OF WATER QUALITY OF NDAKAINI DAM IN
MURANG'A COUNTY, KENYA.**

BY

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FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF THE
DEGREE OF MASTER OF SCIENCE IN ENVIRONMENTAL CHEMISTRY
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OCTOBER, 2022.

DECLARATION

I declare that this is my original work and has not been submitted elsewhere for research. Where other people's work has been used, this has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements.

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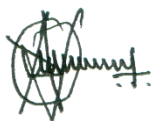
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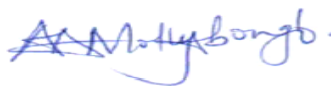


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DEDICATION

This thesis is dedicated to the men in my life; my loving husband Jude Ozioko, the blessed memories of my late father; Fred Ilouno and my cousin Ken Ilouno.

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ABSTRACT

This study assessed the water quality in Ndakaini dam located in Murang'a County to ascertain the physiochemical, biological levels as well as some selected heavy metal concentrations. Assessment was also done on some selected heavy metals in the Ndakaini dam sediment. Sampling was done during dry and wet seasons. Water samples were collected for analysis and the following selected parameters were analyzed; colour, taste, odour, turbidity, electrical conductivity, temperature, total solids, total alkalinity, total hardness, calcium hardness, pH, TDS, TSS, DO, COD, BOD, Si, sulphates, phosphates, chlorides, nitrates, fluorides, nitrites, total coliform and *E. coli* from some selected sites; dam Centre (C), Left edge (Eleft), right edge (Erigh), Thika inlet River (TI), Kayuyu inlet (KI), Githika inlet (GI), Kiama River outlet (KO), Gituru outlet (GO) and Chania Outlet rivers (CO). In both seasons, the study findings showed that most of the physiochemical parameters in all sampling sites tested were within World Health Organization (WHO) and Kenyan Bureau of Standards (KEBS) permissible values except TSS, odour, colour and total coliform. The turbidity (in wet season) and colour levels exceeded WHO standards but are within KEBS standards. In both seasons, the total coliform (2.00 ± 0.00 - 47.00 ± 0.00 cfu/ml) values in all sampling sites did not meet WHO and KEBS limits of non-detectable standard. The biological results for the total coliforms and *E. coli* indicated that the dam was slightly polluted especially at Gituru Outlet (GO) site. When you consider COD and BOD values during dry season, values were higher compared to wet season. In both seasons, the dissolved oxygen (DO) was low at site KO with value of 5.86 mg/L in the dry season and 6.91 mg/L in the wet season. The selected heavy metals analyzed by Flame Atomic Absorption Spectroscopy in water and sediment samples were: Cu, Zn, Pb, Mn, Fe, Mn, Cd and Cr. Water sample result showed that the levels of Pb, Mn, Cr and Fe were higher than WHO guidelines and KEBS limit in most sampling sites. Across all sites, the extent of sediment quality pollution was mainly by Fe while Cu, Pb, Cr, Zn, Cd and Mn were within the recommended levels by the compared international sediment quality guideline used for this study. Statistical processing of data was performed using SPSS software and Microsoft Excel. There was strong correlation between turbidity with sulphate at $r=0.945$, colour with turbidity, TSS, sulphate and phosphate at ($r=0.944$), ($r=0.761$), ($r=0.896$) and ($r=0.783$) respectively in water samples. TDS correlated strongly with nitrate and nitrite at ($r=0.962$) and ($r=0.950$) respectively, fluoride with Zn and Pb at ($r=0.810$) and ($r=0.753$). The sources of pollution in Ndakaini dam catchment may be from the anthropogenic activities carried within the catchment like agricultural activities (farming and animal rearing), effluent discharges from nearby tea processing factories and domestic waste discharges as well.

Table Of Contents

DECLARATION	i
DEDICATION	ii
ACKNOWLEDGEMENTS	iii
ABSTRACT.....	iv
LIST OF TABLES	x
LIST OF FIGURES	xi
LIST OF ABBREVIATIONS.....	xii
CHAPTER ONE	1
INTRODUCTION	1
1.1 Background Of The Study	1
1.2 Statement of the Problem.....	3
1.3 General Objective	4
1.3.1 Specific Objectives	4
1.4 Significance of the study	5
CHAPTER TWO	6
LITERATURE REVIEW	6
2.1 Introduction.....	6
2.2 Water Demand and Resources in Kenya.	6
2.3 Water Pollution: Sources and Causes.....	7
2.3.1 Water pollutants and environmental effects	8
2.3.2 Health risks of contaminated water	9
2.4 Water Quality parameters	10
2.4.1 Physical and Chemical Parameters.....	10
2.4.1.1 Colour	11
2.4.1.2 Odour and Taste	11
2.4.1.3 Turbidity	12
2.4.1.4 Electrical Conductivity (EC).....	12
2.4.1.5 Temperature	13
2.4.1.6 Solids in Water.....	14
2.4.1.7 pH	15

2.4.1.8 Chemical Oxygen Demand (COD).....	16
2.4.1.9 Biochemical Oxygen Demand (BOD).....	16
2.4.1.10 Dissolved oxygen (D.O.).....	18
2.4.1.11 Water Hardness	18
2.4.1.12 Total Alkalinity	20
2.4.1.13 Silicon	21
2.4.2 Nutrients.....	23
2.4.2.1 Nitrates and Nitrites	23
2.4.2.2 Fluoride	24
2.4.2.3 Chloride	25
2.4.2.4 Sulphates	25
2.4.2.5 Phosphates	26
2.4.3 Heavy metals.....	26
2.4.3.1 Manganese	28
2.4.3.2 Cadmium.....	29
2.4.3.3 Zinc	30
2.4.3.4 Lead	31
2.4.3.5 Chromium	31
2.4.3.6 Copper (Cu)	32
2.4.3.7 Iron.....	33
2.4.4 Biological parameters.....	33
2.4.4.1 Total coliforms.....	34
2.4.4.2 E-Coli.....	34
2.5 Sedimentation in Water.....	35
2.6 Relationship of water quality and rainfall variations	35
CHAPTER THREE	37
MATERIALS AND METHODS.....	37
3.1 Description of Study Area.....	37
3.1.1 Features of the Dam	38
3.2 Sampling Sites	38
3.3 Collection and preservation of Sample.....	41
3.4 Laboratory Equipment, Reagents and Apparatus	42
3.4.1 Chemicals and Reagents.....	42

3.4.2 Glasswares and Apparatus	43
3.4.3 Instruments.....	43
3.5 Laboratory Analysis of Samples	43
3.5.1 Determination of Heavy metals.....	43
3.5.1.1 Acid Digestion of Samples for Heavy Metal Analysis	43
3.5.1.2 Preparation of Heavy Metal Standard Stock Solution and Calibration Standards.....	44
3.5.1.3 AAS Analysis of Samples for Heavy Metals.....	44
3.5.2 Determination of physiochemical parameters	45
3.5.2.1 pH	45
3.5.2.2 Electrical Conductivity.....	46
3.5.2.3 TDS.....	46
3.5.2.4 Temperature	46
3.5.2.5 Dissolved Oxygen and Odour	46
3.5.2.6 Colour	46
3.5.2.7 Turbidity	47
3.5.2.8 Total Suspended Solid (TSS)	47
3.5.2.9 Total Hardness	47
3.5.2.10 Calcium Hardness	48
3.5.2.11 Total Alkalinity	49
3.5.2.12 Silicon	50
3.5.3 Determination of Nutrient parameters	50
3.5.4.1 Fluoride.....	50
3.5.3.2 Chloride	52
3.5.3.3 Nitrates.....	53
3.5.3.4 Nitrites	53
3.5.3.5 Sulphate	54
3.5.3.6 Phosphate	54
3.5.4 Biological Parameter Testing	55
3.5.4.1 Total Coliform and E-Coli	55
3.5.4.2 BOD Determination of Samples.....	57
3.5.4.3 Chemical Oxygen Demand (COD) Determination of Samples	58
3.6 Statistical Data Analysis	59
CHAPTER FOUR.....	60

RESULTS AND DISCUSSION	60
4.1 Levels of Physiochemical parameters of water samples in dry and wet seasons	60
4.1.1 Odour	60
4.1.2 pH	63
4.1.3 Total Dissolved Solids (TDS)	64
4.1.4 Electrical Conductivity (EC)	65
4.1.5 Turbidity	66
4.1.6 Colour	68
4.1.7 Total Suspended Solids (TSS).....	69
4.1.8 Total Solids (TS).....	71
4.1.9 Total Alkalinity	71
4.1.10 Total Hardness	72
4.1.11 Calcium Hardness	74
4.1.12 Silicon (Si)	74
4.2 Levels of Biological parameters of water samples in dry and wet seasons.....	75
4.2.1 Dissolved Oxygen (DO).....	77
4.2.2 Biological Oxygen Demand (BOD)	78
4.2.5 Total Coliform and E. Coli (3M Petri film Results) for Dry and Wet season.	80
4.3 Levels of Nutrient parameters of water samples in dry and wet seasons	83
4.3.1 Sulphates	84
4.3.2 Phosphates	86
4.3.3 Chloride	87
4.3.4 Nitrates.....	87
4.3.5 Fluorides	88
4.3.6 Nitrites	89
4.4 Selected heavy metals levels in water and sediments samples during dry and wet seasons	90
4.4.1 Copper (Cu)	92
4.4.2 Lead (Pb)	94
4.4.3 Chromium	95
4.4.4 Zinc	97
4.4.5 Manganese	98
4.4.6 Iron.....	100

4.4.7 Cadmium.....	101
4.5 Person Correlation Result	102
4.6 Discussion.....	107
CHAPTER FIVE	110
CONCLUSIONS AND RECOMMENDATIONS	110
5.1 Conclusions.....	110
5.2 Recommendations.....	113
REFERENCES.....	115
APPENDICES	135

LIST OF TABLES

Table 1.1 Data on the world fresh water resources.....	2
Table 2.1: Status of the main water catchment areas in Kenya	7
Table 2.2: Water Hardness Classification	19
Table 3.1: Significant features of Ndakaini Dam.....	38
Table 3.2 Sampling Sites and Gps Coordinates	40
Table 3.3: Limits of detection and wavelengths for analyzed elements.....	45
Table 4.1: Physiochemical parameters of water samples in dry and wet seasons.....	61
Table 4.2: Physiochemical parameters levels in water samples in dry and wet seasons	62
Table 4.3: Chemical and biological parameters levels in water sample during dry and wet seasons.....	76
Table 4.4: Most Probable number (MPN) of coliform result during wet season	82
Table 4.5 Levels of Nutrient parameters of water samples in dry and wet seasons	84
Table 4.6: Selected heavy metal levels in water samples in dry and wet seasons.	91
Table 4.7: Selected heavy Metal levels in sediment samples in dry and wet seasons.	92
Table 4.8 Pearson correlation of the physicochemical properties of water samples.	102
Table 4.9: Pearson correlation values for the nutrient properties in water samples.....	103
Table 4.10 Pearson correlation of the heavy metal properties of water samples.	104
Table 4.11 Pearson correlation between the physicochemical and nutrient properties of Ndakaini Dam.....	105
Table 4.12 Pearson correlation between the physicochemical and heavy metals properties of Ndakaini Dam .	106
Table 4.13 Pearson correlation between the nutrient parameters and heavy metals of Ndakaini Dam.....	107

LIST OF FIGURES

Figure 3.1: Map of Ndakaini Dam, Study Site (Source: GIS LAB, 2019)	39
Figure 3.2: Sediment collection from site GO	42
Figure 3.3: Fluoride samples analysis (Alizarin method)	51
Figure 4.1: pH levels of water samples of selected sites in Ndakaini Dam.	63
Figure 4.2: Total dissolved solids levels of water samples in selected sites in Ndakaini Dam.	64
Figure 4.3: Electrical conductivity levels of water samples in sampling sites in Ndakaini Dam.	65
Figure 4.4: The Turbidity levels of water samples in selected sites in Ndakaini Dam	67
Figure 4.5: Colour levels of water samples in selected sites in Ndakaini Dam.....	68
Figure 4.6: Total suspended solids levels in water samples in sites in Ndakaini Dam.	70
Figure 4.7: Total Solids levels in water sample in selected sites during wet and dry season	71
Figure 4.8: Total alkalinity levels of water samples in sites in wet and dry seasons.	72
Figure 4.9: Total hardness levels of water samples in selected sites in Ndakaini Dam	73
Figure 4.10: Calcium hardness levels in water samples in sites in Ndakaini Dam	74
Figure 4.11: Si levels in water samples in sites in Ndakaini Dam.....	75
Figure 4.12: Dissolved oxygen levels in water samples in selected sites in Ndakaini Dam.....	77
Figure 4.13: BOD levels of water samples in selected sites in Ndakaini Dam.	78
Figure 4.14: COD levels of water samples in selected sites in Ndakaini Dam	79
Figure 4.15: Temperature Levels of water samples in selected sites in Ndakaini Dam.....	80
Figure 4.16a: 3M Petrifilm analysis of water samples of Ndakaini dam	81
Figure 4.16b: MPN analysis of water samples of Ndakaini dam in wet season, before and after incubation	82
Figure 4.17: Sulphates levels in water samples in selected sites in dry and wet seasons	85
Figure 4.18: Phosphates levels in water samples in selected sites in dry and wet set seasons.....	86
Figure 4.19: Chlorides levels in water samples in selected sites in wet and dry seasons.	87
Figure 4.20: Nitrates levels in water samples in selected sites in wet and dry season	88
Figure 4.21: Fluorides levels in water samples in selected sites in wet and dry season.....	89
Figure 4.22: Nitrites levels in water samples in selected sites in wet and dry season	90
Figure 4.23a: Copper levels in water samples in selected sites in wet and dry season	93
Figure 4.23b: Copper levels in sediment samples in selected sites in wet and dry season	93
Figure 4.24a: Lead levels in water samples in selected sites in wet and dry season.....	94
Figure 4.24b: Lead levels in sediments in selected sites in dry and wet seasons.....	95
Figure 4.25a: Chromium levels in water samples in selected sites in dry and wet seasons	96
Figure 4.25b: Levels of chromium in sediment samples in selected sites dry and wet seasons.....	96
Figure 4.26a: Zn levels in water samples in selected sites in dry and wet season	97
Figure 4.26b: Zn levels in sediment samples in selected sites in dry and wet season.....	98
Figure 4.27a: Manganese levels in water samples in selected sites dry and wet seasons.	99
Figure 4.27b: Manganese levels in sediment samples in dry and wet seasons.	99
Figure 4.28a: Iron levels in water samples in selected sites in dry and wet seasons.	100
Figure 4.28b: Iron levels in sediments samples in selected sites in the dry and wet seasons.	101

LIST OF ABBREVIATIONS

$^{\circ}\text{C}$:	Degree Celsius
A:	Ampere
ADB:	African Development Bank
AOD:	Above Ordnance Datum
APHA:	American Public Health Association
ASAL:	Arid and Semi-Arid Areas.
ATSDR:	Agency for Toxic Substances and Disease Registry
AWSB:	Athi Water Services Board
BOD:	Biochemical Oxygen Demand
BD:	Below Detection
CCME:	Canadian Council of Ministries of Environment.
CETRAD:	Centre for training and integrated research in ASALs Development
COD:	Chemical Oxygen Demand
DO:	Dissolved Oxygen
EDTA:	Ethylenediaminetetra-acetate
EPA:	Environmental Protection Agency
FAS	Ferrous Ammonium Sulfate
g/cm^3 :	grams per cubic centimeter
KNBS:	Kenya National Bureau of Statistics
KEBS	Kenya Bureau of Standards
Ltd:	Limited
m:	Metre
$\mu\text{g}/\text{L}$:	Microgram per litre
m^2 :	Square metre
m^3 :	Cubic metre
mg/kg :	Milligram per kilogram

mg/L:	Milligram per litre
MPa:	Mega pascal
mS/cm:	Milli Siemens per centimeter
NIST:	National institute and Standards and Technology
NGV:	No Guideline Value
NTU:	Nephelometric Turbidity Units
NWRMS:	The National Water Resources Management Strategy
IPCS:	International Programme On Chemical Safety
ISQG:	Interim Sediment Quality Guideline
pH:	Potential Hydrogen
Qmax:	Maximum flow rate
SPSS:	Statistical Package for Social Sciences
TCU:	True Colour Units
TDS:	Total Dissolved Solids
TS:	Total Solids
TSS:	Total Suspended Solids
UNCED:	United Nations Conference of Environment and Development
US EPA:	The United States Environmental Protection Agency
V:	Voltage
WHO:	World Health Organization
WWDR:	World Water Development Report

CHAPTER ONE

INTRODUCTION

1.1 Background Of The Study

Water constitutes approximately 70 percent of earth's surface, making it the earth's most abundant natural resource in the globe. A high percentage of this water is not readily accessible for use by human beings since water is found in various sources, forms and states (Vörösmarty *et al.*, 2000). 97 percent of water on earth is salty, leaving just 3 percent of the total water as freshwater. However, of the fresh water available, only 0.5 percent can be said to be available for use by humans and is mostly found in lakes, rivers, aquifers, streams, as rainfall and in reservoirs such as dams (Baker *et al.*, 2018). The remaining 2.5 percent is found in a frozen state, otherwise, referred to as polar ice and underground water. The demand for water has always increased since high human population growth causes widespread stress on water across the globe. The need for freshwater for use exceeds the amount available. Further pressure on the water for human consumption is caused by social activities that contribute to global warming, alterations of the natural environmental ecosystems, seasonal cyclic changes in climate and weather patterns, among other factors (WWDR, 2018).

The available water for human use is unevenly distributed across the geographic areas inhabited by human beings (Oki & Kanae, 2006). During particular periods when the quality of water is reduced, safe water use by all humans is limited across the globe. Additionally, there is also human misuse of water and water resources which further strains the availability of this water. Contaminated water needs to be sanitized using modern technologies and proper management to prevent plunging almost half the human population from living without enough water by the year 2025 (Maupin *et al.*, 2014).

The data on fresh water resources and quantities are as shown in Table 1.1

Table 1.1 Data on the world fresh water resources

Water sources	Water volume (km³)	Total water (%)
Oceans, Seas and Bays	1,338,000,000	97.4
Ice caps, Permanent Snow and Glaciers.	24,064,000	1.74
Groundwater	23,400,000	0.74
Soil Moisture	16,500	0.0011
Ground Ice and Permafrost	300,000	0.022
Lakes	176,400	0.006
Atmosphere	12,900	0.0009
Swamp Water	11,470	0.0008
Rivers	2,120	0.0002
Biological Water	1,120	0.0001

Source: (Shiklomanov, 1993; USGS, 2019)

According to WWDR (2019), water use has been on the steady increase worldwide at the rate of 1% every year from 1980. This trend is projected to continue at comparable rate until the year 2050. The human activities that are threatening the accessibility of safe water supply to humanity include a high standard of urbanization, which is closely related to industrialization. Moreover, increasing human population and increasing demand for land for agricultural use have also negatively impacted water safety (Wang *et al.*, 2018). The suitability of water from these activities is compromised because of the contamination of water caused by waste materials from the agricultural farms, chemicals and trace metals from the industries and human wastes. Such contaminants make water unsuitable for human consumption, recreation, irrigation and fishing purposes either directly or indirectly due to the bioaccumulation and biomagnification of the contaminants along the food chain, their persistence within the environment and their impacts on animals and plants (Saleem *et al.*, 2019).

Ndakaini dam is the number one source of water supply to Nairobi residents and its environment and attracts its waters from tributaries streaming in from the Aberdare ranges. Three main rivers namely the Thika, Kayuyu and Githika rivers feed the Ndakaini dam; other sources are Kiama and Chania rivers (Hunink & Droogers, 2015). The inlets to and outlets from Ndakaini dam are the principle source of water for agriculture and other activities downstream. The most essential land use activity in Ndakaini is agriculture with inclination towards cash crops (Leisher, 2013), like tea farming.

However, Ndakaini dam faces difficulties of sedimentation and chemical contaminants from nutrients enrichment from these farms, which have led to water degradation. (Leisher, 2013).

Water quality testing is the process of determining the physio-chemical and biological characteristics of water bodies which aids to identify the source of any possible pollution or contamination detrimental to the usage of water (Mishra *et al.*, 2021). Water quality is dependent on two key variables such as temperature and rainfall which affect mobility and dilution of contaminants. Increased temperatures affect chemical kinetics while increased flow leads to a change of stream power hence increase in sediments loads with potential to degrade water quality (Whitehead *et al.*, 2009).

Thus, in this study, water and sediment samples were collected from designated sites within Ndakaini and analyzed as per APHA standards as per required standards as prescribed by APHA (1998), Khanna & Bhutiani (2007), mainly to establish the water quality of Ndakaini dam seasonally.

1.2 Statement of the Problem

Dams are very vulnerable to land use problems and prone to tremendous exploitation (Saytarkon, 2015). Agriculture is the main activity of the inhabitants of Murang'a County and its environs in which the Ndakaini dam is located, with inclination towards cash crop (Leisher, 2013). Tea farming is also common in the catchment area, favored by the type of soil and the weather condition within the region. Farmers use agrochemicals to improve their yields and control pests and diseases. Furthermore, the Chania River which joins the Thika River that feeds Ndakaini dam near the Blue Post Hotel, has been subject of pollution resulting from anthropogenic activities (Gathua, 2015). Ndakaini dam faces difficulties of sedimentation and chemical contaminants from nutrients enrichment, which have led to water degradation (Leisher, 2013).

In addition, increasing industrial growth, urban developments and population growth has led to the establishment of urbanized towns around the catchment area (Oates & Marani, 2017). Thika town is considered one of the fast-growing towns in Kenya and is known for its many industries. There were increasing concerns about the rising effluent volumes from the neighboring towns and shopping centres due to lack of proper sewage system. Polluted water provides a medium for the spread of water-borne diseases. In developing countries, about one million people are affected, mostly children dying yearly either from diseases which includes diarrhea, cholera, dysentery,

hepatitis and typhoid among other conditions, all of which are linked to poor water sanitation (WHO, 2004). Between June and August 2019, cases of cholera outbreak were reported in Nairobi city. These activities might negatively be impacting the quality of water from the dam and associated sediments through inputs of contaminants like heavy metals, among others, leading to alteration of the water physiochemical composition in a way that may be environmentally adverse to the inhabitants around Ndakaini dam.

Additionally, Olum (2008) stressed the urgent need for reliable information for water users, water managers as well as policy makers in Africa on the use and availability of water for adequate planning, prediction and management of water resources.

Therefore, it is highly imperative to regularly assess water quality of Ndakaini Dam supplied to residents of Nairobi and its environs (WHO, 2006).

1.3 General Objective

The primary objective of the research was to evaluate water quality from Ndakaini Dam in Murang'a County, Kenya.

1.3.1 Specific Objectives

Objectives of the research study were to:

- i) To determine the physicochemical and biological quality parameters in the study area by determining colour, taste, odour, turbidity, total solids, total alkalinity, total suspended solids, calcium hardness, temperature, total hardness, Si, pH, TDS, DO, COD, BOD, electrical conductivity, sulphates, phosphates, chlorides, nitrates, fluorides, nitrites, total coliform and E. coli in water from Ndakaini Dam in wet and dry seasons.
- ii) To determine the levels of some selected heavy metals (Mn, Cd, Cr, Zn, Cu, Fe and Pb) found in water and sediment from Ndakaini Dam during dry and rainy season.
- iii) Compare the concentration values obtained for each of these parameters with recommended permissible values from WHO and KEBS guideline Standards for surface and drinking water and sediment quality guidelines (SQGs).
- iv) Assess the possible sources and factors contributing to the pollution along the tributaries in Ndakaini dam.

1.4 Significance of the study

This study will serve to provide a guide to future researchers in assessing the recent water quality data of Ndakaini dam.

The data findings gathered during the course of this research will be crucial to Ndakaini dam management, the Nairobi water and sewerage company to put measures in place to mitigate sources of water pollution for proper management of the dam. The same information will be crucial to the health sector since this dam supplies water to more than 4.6 million people (Ndakaini Brief, 2011).

The information gathered will also be beneficial to environmental management bodies like UNEP, KEBS and NEMA so as to take appreciable measures to strengthen their environmental policies.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

In this chapter, the focus is on areas of interest in determining water quality, including the results from previous areas of focus and research that have been carried out. Additionally, the chapter focuses on specific parameters which are broadly classified as chemical, physical and biological parameters.

2.2 Water Demand and Resources in Kenya

Researches conducted across the Globe show that the supply of water is diminishing as the demand increases. By 2030, it was predicted that the demand for water will transcend its supply by 40% and 50% worldwide and in developing countries respectively (Chellaney, 2013). Mekonnen & Arjen, (2016) reported that in every year, over 4 billion people is prone to water shortage globally. Moreover, it is predicted that 90 percent of 3 billion people from developing nations are going to face severe shortage of safe and clean water by 2050 (UN-Water, 2009). Population increase will ultimately lead to a reduced per capita availability of water (Showers, 2002). Different factors like growth of population, urbanization and development in economy especially in developing countries have exacerbated accessibility of clean water due to inadequacy provision of sanitation services (Engle *et al.*, 2011). If the per capita in water accessibility is less than 1,700 m³ annually, a country is said to be water stressed (Jones, 2014). Therefore, Kenya, country in East Africa, faces water shortage as its per capita in water availability is below 1000 m³ per year. The domestic and industrial water demand in Kenya is always on the rise due to the increasing population and advancement in industrial growth, especially in urban centres. Water demand in Nairobi County is estimated at 750000m³/day against the current supply of 540000m³/day (AWSB, 2012). Accessibility of safe water for human consumption has become a challenge for most rural dweller as they have to travel for about 8 miles in search of clean water, which they end up getting contaminated water at times. (Ondigo, *et al.*, 2018).

According to Jimenez & Asano (2008), best practices should be put in place to ensure that quality and sufficient water supply is realized especially in emerging countries across the globe. The national and county governments are coming up with ways of diversifying availability and accessibility of safe water to the Kenyan population in line with the general world's Millennium

Development Goals and Kenya's vision 2030 (NWRMS, 2007). Construction of Dams to harvest rainwater and tap water from rivers to increase the supply to the residents is one of the strategic plans of these governments (Kenya Vision 2030, 2007).

The natural, renewable water supplies in Kenya are mostly dependent on small and vulnerable catchments covered by montane forests in the country's humid highlands. Table 2.1 depicts the country's top five water towers which include: Cherangani Hills, Mt. Elgon, Aberdare Ranges, Mau Forest Complex and Mt. Kenya. They are, however, the primary sources of numerous rivers in Kenya, which flow into large lakes such as Lake Baringo, Lake Nakuru, Lake Naivasha, Lake Natron, Lake Victoria and Lake Turkana (Crawford, *et al.*, 2012). Nairobi County is supplied with water from Tana River basin which Ndakaini Dam, Ruiru Dam, Sasamua Dam and Kikuyu springs are located. Ndakaini Dam supplies the highest volume of water, about 85% to Nairobi city (Ndakaini Brief, 2011).

Table 2.1: Status of the main water catchment areas in Kenya

Watershed name	Catchment area (ha)	Max. altitude (m)	Gazetted forest area (ha)	Main River
Mt. Kenya	1,253,959	5199	203,145 (4% cropland)	Tana , Athi
Aberdare	1,097,895	4001	104,078 (11% cropland)	Ewsaso Ngiro, Athi
Mau forest Complex	874,746	3098	404,706 (25% cropland)	Mara, Nyando, Yala
Cherangani Hills	212,267	3365	120,841 (19% cropland)	Nzoia, Turkwell
Mt. Elgon	249,996	4320	72,547 (15% cropland)	Nzoia. Turkwell

Source: (Chepyegon & Kamiya, 2018).

2.3 Water Pollution: Sources and Causes

According to Ramakrishnaiah et al., (2009), in the last few decades, demand for freshwater has been on a rapid increase owing to fast-pace growth of population and increase in rate of industrialization. Human practices such as significant urbanization, agricultural practices,

industrialization, and growth of population have impacted in the deterioration of water quality (also known as water pollution) in different continents of the globe (Wang *et al.*, 2010). Most agricultural growth operations, especially those involving increased fertilizer application and filthy conditions have no doubt threatened human health (Okeke & Igboanua, 2003).

Water contamination is usually as a result of two sources: point sources and non-point sources. Point sources of pollution is known to have direct identifiable sources like factory infiltration from a cracked pipe, oil spill from a tanker, sewer discharge, industrial and municipal wastewater effluents. Non-point sources of contamination, on the other hand, are the various origins and methods through which contaminates leach into groundwater or surface water and enter the environment from several non-identifiable sources. Typical instances include runoff from urban waste, agricultural lands etc. Transboundary contamination also occur sometimes, in which pollutants enter the ecosystem in one place and exact pollution effects several miles away. For example, radioactive waste enters through the waters from nuclear reprocessing facilities to nearby nations.

2.3.1 Water Pollutants and Environmental Effects

Polluted water comprises of pollutants which is classified as either inorganic or organic water contaminants. **Organic Water pollutant** are organic materials often referred to oxygen-demanding wastes and are intensely found in the ecosystem. Organic matter originate from sewage, detergents, cosmetics, food wastes, plant waste and so on, having carbon, hydrogen, oxygen, nitrogen and other synthetic elements as major constituents. Organic matter are further categorized into biodegradable and non-biodegradable matter. While biodegradable matter are easily decomposable by organisms, non-biodegradable matter like synthetic organic compounds found in agricultural products (pesticides-insecticides and herbicides) are stable and cannot be easily broken down by organism. Toulene and benzene are one of the toxic non-biodegradable organic compounds discovered in pesticides, solvents, and chemical products. This poses additional challenge during water treatment and in addition, very toxic to humans as well as contaminate aquatic creatures. According to Burks & Minnis (1994), high concentration of organic matter in wastewater can be detrimental to the quality of receiving waters. As organic matters build up in water body, it can give rise to massive growth of plankton or algae, creating a situation called as algal bloom while excessive nutrient in water from fertilizer run off leading to a condition known as eutrophication. These conditions are detrimental to aquatic life by depleting the

dissolved oxygen contents in water, resulting in suffocation and death of fish, odour and deterioration of water quality (Naidoo & Olaniran, 2013).

Inorganic pollutants in water are mainly minerals and ions like; Magnesium, sodium, potassium, zinc, cadmium, copper and lead emanating from residential source like burning practices and non-residential sources like chemical industrial effluents, fertilizers from agricultural run-off, storm water, etc. According to studies carried out, majority of the substances which are inorganic are not easily broken down by organisms and as such very toxic to plants, animals and humans, and may build up over time in the environment because they are stable (Awuah & Abrokwa, 2008). The response to this is by reducing the rate at which they make their own food by the process of photosynthesis. Heavy metals associated with waste waters are often challenging to remove by conventional treatment methods and as such techniques are involved in the removal processes like reverse osmosis, hyper-filtration, electro dialysis, selective ion exchange, etc.

2.3.2 Health Risks of Contaminated Water

One of the key areas that international organizations such as World Health Organization (WHO) focus on in primary healthcare is adequate and safe water provision to communities, with serious considerations given to the developing countries such as Kenya. Consumption of contaminated water mainly through pollution by microbiological and chemical contaminants pose principal human health risks (Oates & Marani, 2017). According to United Nations Conference of Environment and Development (UNCED), utilization of contaminated water causes up to 80% of most diseases, in addition to more than one-third of fatalities. Furthermore, this report indicates that individuals sacrifice up to one-tenth of their productive time battling cases of water-related diseases (WHO, 1997).

In rural areas and farmlands with extensive agricultural activities, overuse of agrochemicals results in considerable levels of these chemicals and pesticides finding their way into the streams and later into the water bodies. Long exposure of some of these chemicals in the form of metals above the permissible limit for consumption pose a great risk to life. Arsenic, for example, is considered hazardous to human health causing cancer of respiratory system, while exposure to lead affects the kidney, central nervous system and blood. Aberrations of chromosomes and damages in the neurological system can be as a result of persistent exposure of mercury. Consumption of food irrigated with effluents containing cadmium can lead to accumulation of cadmium in human body.

Many renal diseases such as nephritis, “itai- itai” and nephrosis were reported in Japan as a result of consuming rice contaminated with cadmium (Friberg *et al.*, 1974).

Adetunde & Glover (2010) argued that uncontrolled faeces contamination finds their way into water bodies increase the pollution. According to Larry (2006), human faeces sheds pathogens which lead to transmission of diseases. Reports show that causer of diseases and death is contaminated ground water (approximately 14,000 people die daily worldwide, majority been the children aged below 5 years). Globally, 1.1 million children die annually because they are more vulnerable to these intestinal pathogens (Steiner & Gurrant, 2006).

2.4 Water Quality Parameters

These parameters refer to the elements of water from which the suitability can be determined and include the biological and physicochemical parameters. Water quality parameters determine the safety and usability of the water. Acceptable limits are set by international standardization bodies. Governments also come up with various standards (WHO, 2013). Some of the parameters in water include colour, taste, turbidity, odour, electrical conductivity, temperature, total hardness, calcium hardness, pH, total dissolved solids, total suspended solids, total alkalinity, total solids, chemical oxygen demand, dissolved oxygen, biochemical oxygen demand, sulphates, phosphates, chlorides, nitrates, fluorides, nitrites, total coliform and *E. coli*.

2.4.1 Physical and Chemical Parameters

The physical parameter as regards to water quality features that are readily measurable and observable that may affect the acceptability of the water for consumption. The physical parameters identifiable in the determination of water quality include; colour, odour, taste, turbidity, electrical conductivity, temperature and presence of solids either dissolved or in suspension.

Chemical parameters of water are used in determination of the chemical content of surface water and are dependent on the source of water or the catchment area (Bhargave *et al.*, 2013). A single exposure to chemical contaminants in water may not have instantaneous health impacts unless there is massive accidental contamination. However, continuous exposure to the chemicals in water may cause adverse health effects (WHO, 2006). The chemical parameters to be analyzed in a water sample includes; pH, COD, BOD, ammonium, nitrates, nitrites and heavy metals (Mn, Cd, Cr, Zn, and Pb).

2.4.1.1 Colour

Water is generally considered to be colourless. However, water appears colourless only when considering water in small quantities. Large water bodies appear blue, with the colour concentration increasing with the increase in depth or distance, a change which is brought by the absorption and scattering of light by the suspended materials (Pope Fry, 1996). There are also easily recognizable changes in the colour of water when soil particles are carried by running water over loose top soil due to erosion. Water is measured in True Colour Units (TCU), and WHO recommendation for colour of water is 15 TCU value since any value not less than 15 TCU can easily be detected by the majority of consumers with water colours below 15 TCU accepted by the consumers. However, the extent of acceptability varies among consumers (WHO, 2006).

The actual cause for colour of water is brought about by dissolved biodegradable organic matter such as humic, lignin and fluvic acid, which are classified as aromatic compound (Drever, 1997). There are acceptable ways of reducing colour from water, ranging from simple methods such as sand filtration to the use of modern technologies (WHO, 2006). Some of the other technologies include hydrolysis by use of alum to coagulate and flocculate, activated carbon adsorption, oxidation and membrane filtration removes the colouration. Various membrane filtration techniques such as reverse osmosis, ultra-filtration and nanofiltration are some of the advanced technologies used to remove soluble organic matter from water (WHO, 2013).

2.4.1.2 Odour and Taste

Water that is used for human consumption should not have detectable odour and taste since their presence in water may create a perception that the water is unsafe for cooking, bathing, washing, and for drinking (WHO, 2013). Odour and taste may result from natural sources such as decomposing vegetation and algae or human sources such as the deposition of human and industrial wastes to the water bodies and through agricultural activities. Detection and measurement of odour and taste are carried out using organoleptic senses; taste and smell. The results are rated in comparison to the threshold odour test, which is considered as the standard control test. The threshold odour test is preferred since it is not a health risk hazard in tasting untreated water, hence it is a convenient method. Due to the close relationship between odour and taste, the removal of odour often results in the removal of tastes (WHO, 2006). The techniques used for odour and taste control includes the use of chlorine dioxide, oxidation, ozone, activated

charcoal and use of potassium permanganate. Generally, there is no particular method used in the removal of odour and taste that has been developed. A combination of techniques is often used (WHO, 2006).

2.4.1.3 Turbidity

Turbidity refers to the extent to which water will lose transparency as an outcome of the presence of suspended particles. The clarity of the water indicates the degree of what amount of suspended particles or materials that are available inside the water. Murkier water is considered to be more turbid than less murky water (Mann et al., 2007). Therefore, turbidity is taken to be a good measure of water quality. There are several factors causing turbidity such as sediments due to erosion, the growth of algae, run-off from rainfall or spillage and discharge from domestic wastes (U.S EPA, 2005). Measuring of turbidity of water is done in Nephelometric Turbidity Units (NTU) using a nephelometer or turbidimeter. The World Health Organization standards require the maximum turbidity not to exceed 5 NTU in potable water (WHO, 2013).

Suspended particles compromise the quality of water and its usability in several ways. Greater level of turbidity influences the aesthetic nature of water that may, in turn, change the perception of consumers. The particles soak up heat and sunlight, thus causing increase in water temperature, reduce the availability of light to the aquatic life and decreases the concentration of oxygen inside the water. The survival of some marine organisms is affected. Suspended particles aid in attachment of toxic organic compounds, pesticides and heavy metals. The process of eliminating water turbidity boosts the costs involved in the process of water treatment (APHA, 1992). Elimination of turbidity is vital in the early processes of water treatment before disinfection is carried out for portable water. No health-based guideline to the acceptable standard limit of turbidity by international regulatory bodies, however the World Health Organization recommends turbidity of less than 0.1 NTU to obtain effective water disinfection (WHO, 2013).

2.4.1.4 Electrical Conductivity (EC)

This can be defined as the capacity of a material/ substance to allow conduction of electric current due to presence of ions and its units are micro milli Siemens per centimetre (mS/cm). The conductive ions may be positive or negatively charged. The level of conductivity indicates the content of dissolved salts in a water sample, for instance; sodium, potassium as well as chloride ions, therefore, it indicates the level of salinity. Conductivity is helpful in determining total

dissolved solids (TDS); that is EC an indicator of the concentration of TDS in the water to avoid separate measurement of each dissolved mineral content (Pradhan *et al.*, 2012). These conductive ions are thought to come from inorganic materials and also from dissolved salts. Carbonate compounds, chlorides, alkalis, and sulfides are some of the key sources of ions in water (Samuel *et al.*, 2023). The EC varies with the number of ions, that is, the more the ions in water the greater the conductivity and vice versa (Gray *et al.*, 2000).

Electrolytes split into negative and positive particles when dissolved in water and the concentration of each anion and cation remain the same. An electrolyte remains electrically neutral even on addition of ions because both the cations and anions are in equilibrium even though the conductivity of water increases (Gray *et al.*, 2000). Deborah & Kimstach (1996) noted that conductivity of water is influenced by presence of dissolved ions such as chloride, phosphate sulfate, and nitrate anions or sodium, aluminum, magnesium, iron, and calcium cations. Temperature has great effect on the conductivity of dissolved solids in water that's the reason the measurement should be carried out under controlled temperature of 25°C. Depending on the constituents of dissolved ions in sewage spills the conductivity of the stream's changes invariably due to presence of some anions (chloride, nitrate, and phosphate). Likewise, the conductivity may be lowered by an oil spill (APHA, 1995). The run-offs, mineral inputs from agriculture and domestic water discharge from the human settlements along the river flows into the water downstream. However, data on the electrical conductivity on streams and sites specific to the Ndakaini dam is limited and it is also not known how electrical conductivity levels within the Ndakaini dam are influenced by anthropogenic activities upstream.

2.4.1.5 Temperature

One of the most readily performed physical assessment of water is the water temperature because it is easy to conduct. Aquatic life is affected by water temperatures when the water is thermally polluted since it affects the survival of different organisms, biological and chemical processes (WHO, 1997). Temperatures also affect dissolved oxygen levels, yet it is required by fish and other aquatic life for survival. Apart from sunlight, aquatic plants also depend on temperature for photosynthesis and animals for metabolism. Thermal pollution occurs due to the introduction of warmer water into a water body. Sources of thermal pollution include urban run-off when watering from tarmacked or paved roads, parking lots, streets, and walkways. Reduced vegetation cover can also result in erosion of heated soil. Once the sediments reach water bodies, they dissipate heat

hence additionally increasing the temperature of the water. The power plants that use water to cool the machines during operations are also a source of thermal pollution when this water is released into the water bodies. Changes in water temperature affects many aquatic organisms. A rise in temperature leads to an increase in their metabolic rate hence increasing the uptake of dissolved oxygen (DO). At the same time, elevated temperatures decrease solubility of gases like oxygen in water (Deborah & Kimstach, 1996). Many lakes and rivers show the rate of change of temperature in towards the vertical as the sun warms the upper layer of water body while the deeper end continues to be cool.

2.4.1.6 Solids in Water

Solids in water comes from different sources like domestic waters, run offs from farmland and as a result, creates siltation problems of dams and blockages of treatment water plants. Total suspended solids (TSS), total solids (TS) and total dissolved solids (TDS) are the main categories of solids in water.

i) Total suspended solids (TSS)

This is about any particles that are found in water that cannot penetrate through a filter during a filtration process (APHA, 1992). The sources of suspended solids include soil erosion, industrial wastewater, sanitary wastewater, aquatic vegetation and organic matter. Suspended solids affect aquatic life by reducing visibility, clogging the gills of fish and by suffocating other aquatic organisms. Additionally, the suspended solids hinder sunlight from adequately reaching the aquatic plants that depend on sunlight for photosynthetic processes. The standard for the amount of suspended solids considered safe for water is between 100-1500 mg/l according to WHO standards (Henderson, 2013; WHO, 2007a).

ii) Total dissolved solids (TDS)

These kinds of solids are regarded as organic and inorganic substances found in molecular, liquid, micro-granular or ionized form and can pass through a filter (often with a pore size of 0.45 micrometers). This parameter is used in ascertaining the quantity of material dissolved in water and quality of water in the streams of water or large water bodies. The presence of a significant amount of TDS in a sample of water can be an indicator of the presence of chemical contaminants. The recommended value of TDS presence in drinking water by WHO is 1000 mg/L (WHO, 2006). Water with TDS value of 600 ppm is considered by WHO to be palatable, with an increase in TDS

values per litre making the water more unpalatable. Water with higher levels of TDS may be rejected by consumers and may cause scaling in household appliances and in water pipes.

iii) Total solids (TS)

Total solid is a term used to refer to solids which are dissolved, suspended and settleable solids found inside of water. Chlorides, calcium, nitrates, phosphorus as well as other ions that can penetrate through a filter with 0.002cm pores can be considered as dissolved solids. Silt, sediments, plankton, satisfactory organic scraps, algae and other particle pollution, which cannot pass via 0.002 cm filters are classified under suspended solids (APHA, 1992).

Total solids in high concentrations make drinking water unsafe and can cause extreme health risks to human beings, terrestrial, aquatic plants and animals (WHO, 2006). The data of total solids obtained in this research will be used as a reference to the impacts of run-offs from the farming practices, wastewater management systems, logging activities and industrial discharges within the catchment areas of Ndakaini Dam.

2.4.1.7 pH

This refers to the measurement of the extent of acidity or basicity in a solution and can be altered by surface run offs. pH is determined by measuring the negative log of hydrogen ions [H^+]. The pH is rated using pH scale, which varies as from 0 to 14. Water with pH level associated with 0 and under seven is classified as acidic, whereas water with a pH of more than seven as basic (WHO, 2012). Usually, water having a pH level of 7 is regarded to be a neutral. Usually, pH of 7 depends on the temperature, which is achieved mainly at 25⁰C. Water which is highly acidic or highly basic is not suitable because of the costs involved in treating such water and the corrosive effects such water has on substances. Additionally, most chemical reactions depend on pH and are therefore affected by extreme pH values. Consequently, biological activities require pH value ranges of 5 to 8 (WHO, 2006).

According to EPA (2001), natural pH in fresh water ranges from roughly 4.5 in acidic, peaty highland areas to over 10.0 in waters with significant photosynthetic activity by algae. However, the most common range found is 6.5-8.0. A high pH changes ionic ammonia to ammonia which is highly toxic to fish (Ongley, 1996). Most heavy metals such as lead become more soluble and more toxic in water as the pH decreases. Metals ionize easily at low pH, enhancing their water mobility and solubility (Reddy *et al.*, 1995).

2.4.1.8 Chemical Oxygen Demand (COD)

This is the needed amount of oxygen required to disintegrate the biodegradable and non-biodegradable organic matter present inside wastewater utilizing a very strong chemical oxidant like potassium dichromate. COD is estimated in laboratories by using a reflux apparatus or digesters (EPA, 1978). Potassium dichromate is reacted with concentrated sulphuric acid (H_2SO_4) along with a silver catalyst. The sample is then refluxed in this blend for two hours following which the consumption of the chemical oxidant can be linked to the equivalent oxygen demand. Chemical Oxygen Demand test has advantages over the BOD test. COD test is a simpler and quicker test compared to the BOD test since the duration required for the COD test is only 2-3 hours, whereas the BOD check requires five days. COD measures every single organic contaminant, including biodegradable contaminants. The COD check also oxidizes materials which microorganisms are not able to metabolize in 5 days.

There exists a relationship between BOD and COD for a specific sample. However, the connection is established empirically. The COD value obtained can be utilized to approximate the BOD of a particular sample. Toxic compounds, for example; heavy metals and cyanides present in the samples to be analyzed do not impact the oxidants utilized in the Chemical Oxygen Demand test. COD test can give an indication of the strength of wastes that contain high levels of toxicity for the BOD test (EPA, 1978). However, a number of organic molecules such as benzene and pyridine are to some extent resilient to dichromate oxidation and may offer low COD levels than the actual levels present in the water being tested. COD measurement is often carried out utilizing a strong oxidant placed under acidic circumstances. There is an addition of an excess quantity of a known oxidant to the sample. The calculation of the concentrations of organics in the sample can then be done once oxidation is complete. The calculation is done by determining the remaining quantity of oxidant inside the solution. This is mostly carried out by titration using a potentiometric indicator such as orthophenanthroline ferrous complex. The expression of COD is done in mg/L unit, which points out about the mass of oxygen that is consumed per litre of solution (EPA, 1978; Clair *et al.*, 2003).

2.4.1.9 Biochemical Oxygen Demand (BOD)

This is the proportion of the measure of dissolved oxygen used by microorganisms in a certain pool of water to decay organic matter in a given water sample. The amount of oxygen that the

organisms consume within a time frame and at a designated temperature is determined using a BOD test. BOD test is usually applied to establish the degree of organic pollution of water and is carried out for a duration of five days at a temperature of 20 °C (Apha, 1992). BOD test measures the biodegradable fraction of water sample which is commonly made up of organic wastes like grass clippings, and manure (Gray, 2004.) Additionally, BOD can be used as a measure of wastewater treatment plant effectiveness. Factors that affect the rate of oxygen consumption in a certain water sample include pH, temperature, varieties of organic and inorganic substances available inside the sample and the kinds of microorganisms present in the sample. Higher values of BOD indicate rapid rates of oxygen depletion in the water source from which the sample for testing is obtained. This in turn is equated to the low amount of dissolved oxygen present in the water source available to aquatic species. High BOD level and low dissolved oxygen are harmful to aquatic life in that they cause these organisms to be stressed, suffocate and die.

BOD measurement is usually carried out using two sets of samples from each sampling points. One of the samples will be tested instantly for dissolved oxygen, whereas the second sample will be incubated for five days in an unilluminated shade, with a temperature of 20 °C before the remaining amount of dissolved oxygen is tested (EPA, 1978). The difference between the initial value obtained in the first test as well as the second test stands to be the BOD value expressed in milligrams of oxygen per litre, representing the organic matter available inside the sample all through incubation. In instances when the oxygen level results obtained after the 5-day incubation is zero, indicating high levels of organic pollution. It is impossible to determine when the zero points are obtained within the 5-day incubation period; hence, it is not possible to determine the BOD level of that sample. This challenge is overcome by diluting the original sample with dilution water and by a factor that will yield at least a minimum final dissolved oxygen level of 2 mg/L (WHO, 2006). It is necessary to have enough microorganism, which can oxidize the biodegradable organic matter in the water sample. Usually, domestic waste-water, un-disinfected effluent waste water do have satisfactory microbial populations, however, water samples that contains insufficient microbial population like untreated or disinfected industrial wastes are first seeded with microorganisms (Lenore *et al.*, 1999). The purpose of biological oxygen demand (BOD) is similar to that of chemical oxygen demand (COD) in that both quantify the quantity of organic chemicals in water. COD, on the other hand, is less specific since it assesses everything that can be chemically oxidized rather than simply amounts of biologically active organic matter.

2.4.1.10 Dissolved Oxygen (DO)

This is a measure of the volume of dissolved gaseous oxygen (O₂) available in the water. It is one of the vital water quality parameters since it influences the living organisms within a particular water body. Too high levels of dissolved oxygen affect water quality, and too low levels are also harmful to aquatic life (APHA, 1992). Aquatic organisms depend on dissolved oxygen for respiration. Bacteria and fungi are some of the microbes that also depend on dissolved oxygen for microbial activities that are important in the decomposition of organic material for purposes of recycling nutrients. Temperature and pressure affect dissolved oxygen. The concentration of dissolved oxygen reduces with the increase in temperature and falls with a decrease in pressure. At high altitudes, the dissolved oxygen concentration is low because pressure decreases with increase in altitude. The dissolved oxygen in surface waters is usually in the range above 6.5-8mg/L and decreases at higher temperature (Kumar *et al.*, 2020). The oxygen supply can be refilled in an environment where there is proper mixing of air (good aeration) and in rapid flowing streams whereas in standstill water courses, the atmospheric oxygen diffusion in water is low, showing that the available oxygen is quickly used up (Thomas & Williams, 2003).

There is no recommended threshold value of DO in water by WHO (2006).

2.4.1.11 Water Hardness

This is defined as water containing a high amount of dissolved mineral content, mostly magnesium and calcium. Water hardness is thought to be caused by the presence of other dissolved ions not only by magnesium and calcium but also by the presence of iron, zinc, strontium, iron, aluminum as well as manganese. Some monovalent ions of potassium and sodium don't lead to water hardness but the divalent salts form stable ions with anions which leads to total hardness (Sengupta, 2013). There are two types of water hardness formed thereof: non-carbonate and carbonate hardness. Non-carbonate hardness is also referred to as permanent hardness since it cannot be broken by boiling unlike the carbonate hardness where its bonds are weak. Hardness is often introduced into groundwater as water percolates through minerals containing calcium or magnesium. The most common sources of hardness into water bodies are limestone (which delivers calcium into the water) and dolomite (which introduces magnesium) and as such, the hardness level in groundwater is higher than that of surface water (Sengupta, 2013).

Hard water poses a lot of challenges to consumers by forming scum with soaps, staining of clothes, scaling of electric water heaters and boilers, reduces lathering of soaps, clogging of hot water pipes

used to distribute water and staining of teeth when consumed as drinking water. As classified below in table 2.2, when water does not lather or foam easily with soap, the water is termed a hard water.

Table 2.2: Water Hardness Classification

Content of calcium carbonate equivalent (mg/L)	Hardness Classification
0 to 50	soft
51 to 100	Reasonably soft
101 to 150	Slightly hard
151 to 250	Moderately hard
251 to 350	Hard
> 350	Very hard

Source: Schutte (2006)

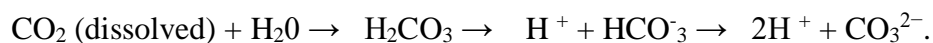
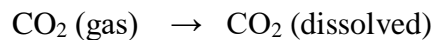
The hardness of water can have health implications since it is used both at industrial and domestic levels. Research carried out in England and Wales shows that there was an increase in cardiovascular disease due to intake of hard water (Crawford *et al.*, 1971). Exposure to hard water has been reported to be a risk factor that could worsen eczema. Other health effects associated with excess/deficiency in intake of calcium and magnesium include obesity, osteoporosis, rectal cancer, kidney stones, hypertension, coronary artery disease and stroke and insulin resistance (WHO, 2010). According to Wang *et al.*, (2018), water hardness can be determined by the use of different methodologies like the use of Disposable MEMS-Based electrochemical sensors. Another way of determining water hardness is the use of complexometric and colorimetric concepts (Bhattacharjee *et al.*, 2013).

According to the research conducted in Kalundu streams and Kalundu dams in Kenya to assess the water quality, the levels of hardness were well below the set limit by the World Health Organization. The highest levels of hardness were 451.67 ± 29.94 mg/L as compared to the set limit of 500 mg/L by WHO (Nzeve & Matata, 2021). Another retrospective study carried out in Ethiopia shows that the levels of hardness in their water was above the recommended limit therefore posing a health risk to the consumers (Alemu *et al.*, 2015).

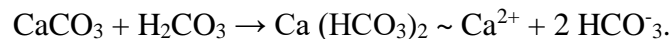
2.4.1.12 Total Alkalinity

The ability of water to take positive charges is defined as its alkalinity. Generally, it is a measure of water's buffering capacity, or the quantitative ability of bases in water to neutralize acids.

Waters with minimal alkalinity (such as rainwater or distilled water) are extremely sensitive to pH changes; a reduction in pH can occur with only a little addition of an acid or base. Water's ability to tolerate pH fluctuations develops as alkalinity increases, hence increasing its buffering capacity (Martinez-Alvarez *et al.*, 2018). That is, water with a high alkalinity may withstand high concentrations of acids or bases without dramatically altering its pH. Bicarbonate (H_2CO_3) and carbonate (CO_3^{2-}) are the primary buffering bases in natural waters, although other weak acids such as borate, silicate, and inorganic acids may also contribute to alkalinity (Julian Trick *et al.*, 2018). Carbonic acid (H_2CO_3) is formed when carbon dioxide (CO_2) dissolves in water. It dissociates and is in equilibrium with bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions:



When an acid is given to water, the concentration of hydrogen ions increases, which interacts with both the carbonate and bicarbonate ions, shifting the equilibrium to the left and releasing carbon dioxide into the atmosphere. The extra hydrogen ions will be absorbed by readjustment of the equilibrium equation as long as there is bicarbonate and carbonate present. The addition of acid will therefore induce a reduction in pH only after all of the carbonate and bicarbonate ions have been depleted. Natural carbonates such as CaCO_3 (limestone) that breakdown when acidic rain water comes in contact with watershed soils or the stream bed replenish the quantity of bicarbonate in water. CaCO_3 dissolves to generate calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$), which dissociates and raises the concentration of bicarbonate in the water.



According to Fritz (1994), biological activity may modify the alkalinity of a water sample during storage, or excessive CO₂ loss may cause CaCO₃ precipitate in the sample container. In carbonate terrains, the alkalinity sample may need to be filtered since there may be suspended calcite particles that cause an overestimation of the result.

Titration with the amount of mineral acid necessary to reduce the pH in a water sample to a given endpoint by colour or electrometrically determines alkalinity. The consumption of bicarbonate in solution is marked by an endpoint of roughly pH 4.5 and the data are commonly given in milligrams CaCO₃ per liter (Julian Trick *et al.*, 2018).

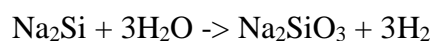
Titrations of total alkalinity and phenolphthalein alkalinity are useful for calculating chemical doses necessary for natural water treatment. Carbonate, hydroxide, and bicarbonate stoichiometric relationships are only true in the absence of considerable quantities of weak acid radicals other than carbonate, hydroxyl, or bicarbonate. Furthermore, there are interferences to measuring alkalinity accurately; free accessible residual chlorine greatly impacts the colour response of the indicator in some water sources through bleaching action.

Alkalinities in poorly buffered water may be less than 40 mg CaCO₃/L, but alkalinities in water tested from a stream flowing through a limestone or "karst" zone may be higher than 200 mg CaCO₃/L. Hinga (2002), mentioned that the alkalinity of most lakes as well as rivers ranges between 100 and 5000 µeq l⁻¹ and the pH ranges between 6 and 9. For comparison, seawater is typically pH 8.2 with an alkalinity of about 2300 µeq l⁻¹. USEPA has not yet formulated the maximum alkalinity values for sewage effluents or drinking water, however, high alkalinity causes water to have a bitter taste. Nevertheless, the key concern regarding water alkalinity is about the reactions that could take place between alkalinity and certain cations present in water (Bozorg-Haddad *et al.*, 2021).

2.4.1.13 Silicon

After oxygen, silicon is the second most plentiful element, accounting for roughly 25% of the earth's crust and classified as a metalloid. Silicon exists in compound form as silica (SiO₂) rather than in its natural elemental forms. Silica which is also called silicon dioxide is a form silicon which is mostly known. It can exist as amorphous or crystalline forms. The forms of silica in crystalline structure are inter related with pressure and temperature. They include: cristobalite quartz and tridymite. As a result of its amount in the tropical locations found in various minerals, it forms a major chemical constituent of natural water bodies (Gbadebo *et al.*, 2013). Silicon

concentration is 30 ppb in the surface layers of oceans, and about 2 ppm silicon in deeper water layers. Rivers, commonly contain 4 ppm silicon. According to Jansen et al. (2010), silicate minerals in sediments and rocks find their route to the natural water sources where they dissolve. According to Georg et al. (2006), a lot of silicon is transported to the sea of which less amount of dissolved silicon is eliminated from the rivers by the processes of chemical or biological transformation. Different compounds of silicon react with water to form other complex compounds. For instance, SiF_4 reacts with water to form HF while the reaction with SiCl_4 is very violent (Venturini *et al.*, 2013). Studies show that silicides of transition metals are less reactive as compared to first and second group members as illustrated below;



In the equation above, hydrogen and /or silanes are produced as typical products (Borisenko, 2013). The solubility of silicon compounds differs greatly, for example, SiO_2 is partly insoluble in water as compared to other minerals (Martin, 2013). Mica, olivine, perlite and talc are different minerals that contain silicon in quantifiable amounts, moreover, gemstones are composed of silicon (Christidis, 2011).

Silicon finds wide application in construction and industrial sectors. It is used as a aid in chemical, steel and electron industries. Rubber and other resin like compounds are key silicon compounds used in industries because they can withstand processes involving oxidation and chemical weathering (Abd *et al.*, 2014). They also serve lubrication role especially under very high temperatures (Vinceti *et al.*, 2013).

Silicon plays a significant role in the ecosystem especially in growth of plant. Silicon is necessary in increasing the stability of plant species like bamboo and dandelions. High levels of silicon may limit the rate of algae growth (Liang, *et al.*, 2015). Silicon in the diet of animals help strengthen their skeleton and development of bones especially to rats and chickens (Vasanthi *et al.*, 2012).

High exposure of silicon is associated with ill health effects. Studies have shown that silicosis (disease of lungs caused by accumulation of airborne crystalline forms of silica in the lungs) may be caused by fine particles of silicon compounds. Silicosis, which is a typical profession related illness for example mine workers or stone grinders (Hoy & Chambers, 2020). The severity of silicosis depends more on the length of time and amount of exposure to inhalation and hence can render humans more susceptible to lung cancer and tuberculosis. It can also lead to eye, nose and

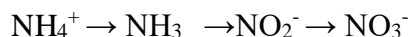
throat irritation (Silicon tetra chloride) (Pandey & Agarwal, 2012). Research carried out in Nigeria shows appreciable amounts of dissolved silica in drinking water. The increased levels might have been due to weathering process taking place. There are no set standards for silica in portable water (Gbadebo *et al.*, 2013).

2.4.2 Nutrients

Waste water that end up discharged into the rivers and streams often contain large amount of nutrients. In severe cases, these excess nutrients in water lead to eutrophication of the water bodies; a situation where enrichment of water bodies with nutrients leads to excessive growth of aquatic plants like algae, duckweed, cyanobacteria and so on. When these aquatic plants die and are decomposed by aerobic bacteria, dissolved oxygen in the water body becomes depleted which in turn become detrimental to the survival of oxygen dependent, aquatic species like fish.

2.4.2.1 Nitrates and Nitrites

These are ions that occur naturally due to the nitrogen cycle. Nitrogen exists as nitrate, ammonia, nitrite and also organic nitrogen. The common form of nitrogen in natural waters is Nitrate ion (NO_3^-). Nitrate ion (NO_3^-) results from either nitrification or oxidation process, which is the stepwise addition of oxygen atoms to nitrogen atoms (Wolfgang *et al.*, 2002) as shown below:



Nitrate ion is mainly found in inorganic fertilizers. Leaching and surface water runoff through agricultural lands, human and animal waste contaminations like sewage and waste water discharge are some of the sources that increase the concentration of nitrates into the water bodies (WHO, 2006). Nitrite (NO_2^-) oxidizes into nitrate after entering an aerobic regime (Deborah & Kimstach, 1996). Nitrites normally exist in very low concentrations because it is the intermediate between ammonium and nitrates. Nitrate levels of over 5 mg/L in natural waters normally indicate anthropogenic pollution and 200 mg/L is an extreme level. Nitrite ions (NO_2^-), such as sodium nitrite are used to preserve food. Ammonia exists in water as either ammonium ion (NH_4^+) or ammonia gas (NH_3). That is to say; Ammonia mainly exists in ionized form (NH_4^+), however, at high temperature and high pH level, the ionized ammonia changes to un-ionized ammonia gas (NH_3). Ammonia is more harmful to freshwater aquatic life and fish (Ongley, 1996). Presence of ammonia can lead to oxidation, especially in anaerobic conditions resulting in formation of nitrite

ion, that is to say that in aerobic systems, ammonia can easily be broken down by nitrifying bacteria to form nitrite and nitrate.

Ingestion of 10mg/l of nitrate and nitrites can lead to the blue-baby syndrome (Skipton & Hay, 1998) and infants are usually the most affected. At the same time high levels of oxidized nitrogen lead to eutrophication, which leads to excessive algae growth that eventually decreases dissolved oxygen levels in the water (Murdoch *et al.*, 2001). In drinking water, the guideline value for the nitrate content is 50 mg/L while that of the nitrite content in drinking water is 3 mg/L (WHO, 2006).

2.4.2.2 Fluoride

Fluoride ions are found in various minerals and can be present in water. Its functions includes enhancement of the resistance profile and strength of tooth enamel surface. Fluoride is a mitogen for osteoblasts and stimulates bone formation. Crippling skeletal fluorosis often develops as a result of drinking-water containing fluoride level over 10 mg/L. There exists a clear proof from India and China stating that daily consumption of 14 mg of fluoride leads to an elevated danger of bone fractures and skeletal fluorosis. An assessment by the US National Research Council in 2006 backs up this conclusion.

The tea plant, (*Camellia sinensis*L.) is a prevalent accumulator of fluorine compounds, which are released upon forming infusions like the common beverage. Fluoride is the most bio available form of fluorine, and as such, tea is a potential channel for an overdosing of fluoride (Chan *et al.*, 2013). Nearly, 50% of absorbed fluoride is discharged via the kidney within twenty-four-hour period. The rest can be retained inside the oral cavity, as well as in the lower digestive tract. Food fasting significantly boosts the rate at which fluoride is absorbed to near 100%, when taken with food (Mcdonagh *et al.*, 2000). It had been discovered that consuming one litre of tea daily, can possibly provide the everyday allowable intake value of 4 mg each day. The research indicated that tea consuming communities are at a greater danger of dental as well as skeletal fluorosis, in the case where water fluoridation is in effect (Mcdonagh *et al.*, 2000). Small doses of fluoride ion in the mouth minimizes enamel and tooth decay (Griffin *et al.*, 2007). It is one of the ingredients utilized in toothpaste and also in water fluoridation to lessen rotting of the tooth. The impact resulting from an increased doses and frequent exposure to fluoride can be very toxic and may cause serious health complications. The Guideline value that has been set for fluoride is 1.5 mg/l.

2.4.2.3 Chloride

Chloride is a main mineral component, largely found in all forms of water. Chloride inside of water solutions is typically in the form of potassium, sodium, and calcium salts. It is present in very minor concentration in natural as well as unpolluted water. Chloride in higher concentrations results in an undesirable taste to water (KDHE, 2008). In addition, high chloride concentrations are corrosive to metals in the water distribution system, especially in waters with low alkaline content (Pradhan *et al.*, 2012). Some of the sources where Chloride in drinking-water originates from natural sources, urban runoff, industrial effluents and sewage. The main source by which humans are exposed to chloride is through addition of salt to foods. Chloride in excess concentrations of approximately 250 mg/l can lead to undesirable taste in water. The World Health Organization had set a guideline value for chloride to be 250 mg/l.

2.4.2.4 Sulphates

Sulphates is one of the naturally occurring minerals which are utilized commercially, in the chemical industry. Sulphates are released into water through industrial wastes products as well as through atmospheric deposition. However, most elevated levels often occur in groundwater. Generally, the average daily consumption of sulfate via, air, drinking water and food is around 500 mg per day, with meals being the primary source. Nevertheless, in instance where the drinking-water supplies contain significant amounts of sulphate, drinking-water may become the primary method of consumption.

Marine algae produce and accumulate excessive concentrations of Sulphur compounds greater than most terrestrial plants because the habitats they live in are mostly characterized by restricted nitrogen and rich Sulphur supply such as underground volcanoes (WHO, 2004). The biogenic Sulphur when come into contact with seawater converts to sulphate ions. However, due to the gastrointestinal impacts that emanates from intake of drinking-water having excessive level of sulphate, it is advisable to call in health authorities if drinking water contains sulfate concentrations of more than 500 mg/l. Sulphate in drinking water can also possibly cause recognizable taste disparity and can lead to corroding of distribution systems (WHO, 2003). There is no guideline value for sulphate.

2.4.2.5 Phosphates

Phosphorus is abundant in nature and may be found in plants, microorganisms, animal feces, and household waste. It is an essential nutrient to living organisms and occurs naturally in water bodies, mainly in the form of phosphates (Kroiss et al., 2011). It also exists in waste water in the forms of soluble orthophosphate ion (PO_4^{-3}), organically –bound phosphate and other phosphorous-oxygen compounds. Domestic and industrial discharges, sewage, agricultural run-offs including unutilized fertilizers, and changes in land use in places where phosphorous is naturally plentiful in the soil are all sources of phosphates in the surrounding. Phosphate contamination produces eutrophication of a stream, in which algae and aquatic plant development quickly absorb oxygen (Ongley, 1996; Kenneth & Neeltje, 2002). Phosphorus that enters such bodies of water, combined with nitrogen as nitrate, stimulates the growth of algae and other plants, resulting in massive blooms, slimes, and diurnal dissolved oxygen changes (Gerardi, 2003). According to US EPA the recommended intake of phosphate in drinking water is 0.1 mg/L (US EPA 1986). High concentrations of phosphate have tremendous health effects which include: kidney failure, damage of the muscles and breathing problems (Nyamangara *et al.*, 2013).

It has not been established whether the levels of phosphorous flowing from river into Ndakaini dam are due to the human settlements and related human activities.

2.4.3 Heavy Metals

Trace metals are contaminants which are hazardous mostly to the aquatic and terrestrial organisms, human beings included. The long-time health risks of the continued exposure of the trace metals include reproduction defects, damage to organs such as liver and kidney, anomalies in growth and development, disorders in the nervous system and risk of cancer to humans (Singh & Kumar, 2017). Human beings are exposed to these contaminants directly or indirectly. The direct exposure is when humans consume contaminated water as drinking water. Contamination through skin contact also takes place when bathing or swimming in contaminated water. The indirect health risks include consumption of agricultural food items that have been grown using contaminated water. An example is fish consumption. Through bioaccumulation and biomagnification, humans are indirectly affected by these contaminants as they move along the food chain to reach the human digestive system (Yuan *et al.*, 2014).

Metals are some of the major global environmental pollutants. Water is a very important resource that plays a major role in giving life and sustaining living organisms. Water finds numerous applications not only for drinking purposes, but also for recreational engagements like fishing, livestock, and irrigation for farming and energy purposes. The principal source of water to the dams and the habitats to living matters is through rivers. Many researchers have indicated that among other factors such as increasing population, industrialization, urbanization, one of the dominated anthropogenic practices around the rivers is agriculture. These anthropogenic activities around rivers not only affect the quality of water, making it unsafe for human utilization but also alters its physio-chemical composition through the introduction of high quantity of nutrients which heavily pollute the river, leading to the damage of the biotic environment (Singh & Kumar, 2017).

Heavy metals are common surface water pollution which enters aquatic system as trace elements through anthropogenic activities such as domestic waste water, industrial discharge, waste water treatment and fertilizers. Conversely, metals may enter into aquatic system naturally, through airborne dust, leaching of rocks, wild fires and vegetation (Fernandez & Olalla, 2000). Heavy metals in surface water and sediments have been recorded in rivers. Sediment in aquatic environments, act as sinks for the heavy metals owing to other factors such as sedimentation, dilution, and precipitation (Duncan *et al.*, 2018). It has also been extensively noted that heavy metal concentrations in sediments can be several orders of magnitude higher than in water. Sediments related heavy metals presents a direct risk to benthic creatures, and also a lasting cause of pollution to higher trophic organisms.

Heavy metal ions need to be removed from the environment and in particular the water bodies to prevent such ions from entering the food chains. Such preventive measures will ensure that the harmful effects of such heavy metal ion are eliminated (Gavrilescu, 2004).

The first process in heavy metal determination is digestion of the metal of interest prior to analysis by spectroscopic means. Digestion of metals aids in reduction of interferences by organic matter and to convert metal related to particulate to a form that is easily determined by either inductively coupled plasma spectroscopy (ICPMS) or by AAS. Close and open system types of digestion are usually in place in digestion process. Open digestion includes dry ashing, nitric acid digestion, nitric acid-sulphuric acid digestion, nitric acid –hydrochloric acid digestion and nitric acid – perchloric acid digestion. “Closed system digestion involves microwave assisted digestion”

(Ozturk et al, 2009). Nitric acid is adequate for easily oxidized material and will digest most samples adequately but some samples may need addition of either perchloric, hydrochloric or sulphuric for digestion to complete totally. APHA (1998) noted that “dry ash formation is helpful if large amounts of organic matter is present”.

Atomic absorption spectroscopy (AAS) is an analytical technique that employs the use of absorption spectrometry to determine the concentration of heavy metals in a sample, and can determine over 60 elements in sample solution being analyzed. It requires standards of known analyte content to establish the relationship between the measured absorbance and the analyte concentration in accordance to Beer-Lambert Law.

Beer-Lambert law states that the electrons of an atom in the atomizer can be excited to higher orbitals (that is the excited state) for a short duration of time by absorbing a defined quantity of energy in the form of radiation of a given wavelength. Each wavelength matches to one unique element and the width of an absorption line is only in the range of a few picometer, which determines the selectivity of the element.

According to APHA (1992), in flame atomic absorption spectrometry, a sample is allowed to aspirate to the flame and broken down into atoms by the process of atomization. The monochromator receives light beam from the flame which passes through the detector which measures the quantity of light absorbed by the element atomized. It maintained that for “some metal, the atomic absorption exhibits superior sensitivity over flame emission. Because each metal has its own unique characteristic absorption wavelength, a source lamp composed of the elements is used for each metal. This makes the method comparatively spectral or radiation interference free. Lenore et al. (1999) added that “most atomic absorption instruments are equipped for operation in an emission mode, which may provide better linearity for some elements.

2.4.3.1 Manganese (Mn)

This is most commonly found ion in soils and groundwater. It is incredibly abundant in the earth's crust and mostly available in mixture with iron ores and over 100 other minerals. Manganese can also be found in the atmosphere as particulate suspensions. It is a crucial component of biological systems whose chemical interactions is majorly determined by pH, oxidation and reduction processes (Shand *et al.*, 2007). Manganese is, however, not found in its elemental form. Manganese ionizes in a chemical reaction to form manganese (II) ions (Mn^{2+}) and manganese (III)

ions (Mn^{3+}). The Mn^{2+} ion is more soluble than Mn^{4+} ; therefore, manganese tends to be more bioavailable with lessening pH and redox potential (Heal, 2001). Presence of manganese in water can occur either in suspended or dissolved forms and can also be found in soil with respect to the organic content and the pH of the soil (WHO, 2011a).

In aquatic systems manganese of levels greater than 1.5ppm cause growth inhibitions and total chlorophyll reduction in algae (Fargašová *et al.*, 1999). Content of manganese ions in water at 0.1 mg/L cause undesirable taste. Concentrations of manganese of 0.02 mg/L and above can result in chemical reactions that form coatings in water pipes. Manganese consumption in small quantities and its natural forms is not harmful to plants and animals. However, constant exposure to manganese at high levels can cause neurological effects, especially when inhaled, causing Parkinson-like syndrome (WHO, 2011b). Analytical methods of the presence of manganese inside of water include AAS and inductively coupled argon-plasma optical emission spectrometry (ICP-AES). This can determine the quantity of manganese as low as 0.01 μ g/L. The recommended acceptable value of manganese ion content in water that is drinkable by WHO is 0.01 mg/L (WHO, 2006). The untreated waste water discharges and run off from agricultural farms along the tributaries may be discharging manganese into the water. However, level of manganese in the water and sediments of Ndakaini dam have not been quantified.

2.4.3.2 Cadmium

Cadmium occurs naturally in soils, rocks and coal. It is soluble in acids but not in alkaline and forms complex compounds. The anthropogenic activities related to cadmium pollution are application of mineral fertilizers and industrial discharges such as paints, plastics which get into aquatic systems through surface run offs (Roberts, 2003). Cadmium also enters the water through the industrial discharge or deteriorated galvanized pipes, very much expected as cadmium is predictable by-product of zinc, also of palladium and copper.

There are various health effects of Cadmium ion and also, it is a danger to the environment. It is considered carcinogenic to humans. Exposure to cadmium is through ingestion or inhalation but mainly through food and can cause respiratory tract infection and kidney problems which can be fatal if not attended to in time. Cadmium compounds are also carcinogenic, and exposure to human can cause weakening of the bones, which can eventually lead to bone fracture. Even at concentrations as low as 1 μ g/l cadmium inhibits the growth of some species of phytoplankton

(Bryan & Langston, 1992). In aquatic ecosystem, cadmium can bio accumulate in fish, shrimps, lobsters, oyster and so on.

The US EPA did set a maximum content of Cadmium (Cd^{2+}) as 0.005mg/L. This agency set the standard after it discovered the health risks of exposure to Cadmium, including nausea, vomiting, diarrhea, muscle cramps and renal failure among other effects (Rahimzadeh *et al.*, 2017). The WHO gives a guideline value of cadmium in drinking water as 0.003 mg/L (WHO, 2006). Different methods have been designed to examine the level of Cadmium in water such as spectrophotometric method (Dithizone method) and polarographic method. (ISO 1986; Ware 2010). The guideline value of Cadmium according WHO is 0.003 mg/l (3 μ g/l). The levels of cadmium in an aquatic system should be closely monitored because it is highly toxic to aquatic life (IEPA, 2001).

2.4.3.3 Zinc

Zinc ion has a mass of 65.4g/mol, it is an oxidizing agent with electrochemical equivalent of 1.09g/AH. Zinc undergoes ionization to Zinc (II) ions (Zn^{2+}). Zinc and its ions are only slightly soluble in water and can readily be found in water in small concentrations when erosion occurs on rocks and soils (Wang *et al.*, 2018). However, high levels of zinc in water can occur. In such high concentration, there should be higher concentrations of other metals in the same water, such as cadmium and lead. Zinc is also found in plumbing materials like water pipes and galvanized roofing materials. Its main source in water is commercial inorganic fertilizers (Mortvedt, 1995).

Zinc does not have harmful effects on human health when consumed in low concentrations but high levels of zinc in water may cause nausea, vomiting, stomach upset and other related problems (Pradhan *et al.*, 2012). Also, copper deficiency and anemia are associated with high intake of zinc in the body as it interferes with iron and copper metabolism (US EPA, 1980). However, zinc is useful for various metabolic processes like cell development, embryonic development as well as important for semen production in males. Water that contains Zinc ions more than 3-5mg/L forms a greasy film when boiled. Water containing zinc levels above 5mg/l has an objectionable taste, causes adverse effects on growth, survival and reproduction in aquatic life (Eisler, 1993).

Continued use of inorganic fertilizers and domestic waste at the Ndakaini dam regions may lead to accumulation of zinc in rivers through run offs and leaching, which eventually interfere with

aquatic systems. It is not known whether the zinc levels in the Ndakaini dam Basin are associated with anthropogenic activities.

2.4.3.4 Lead (Pb)

Lead is considered typically, as the most plentiful and common heavy metal found in the earth's crust, accounting for 13mg/kg of the overall mass of the earth's crust. Lead can be found in nature in stable isotope form as ^{208}Pb , ^{206}Pb , ^{207}Pb and ^{204}Pb , arranged in their order of abundance (WHO, 2011c). Lead undergoes ionization to form Pb^{2+} and Pb^{4+} ions when forming chemical compounds during reactions. Various applications of lead include; in the manufacturing of solder, ammunition, rust inhibitors, paint pigments. Lead is a key constituent component of lead-acid battery used in making of car battery (WHO, 2011c). Traces of lead can be found in water from erosion of dissolved ores in soils and rocks. Household plumbing systems with lead content can also be sources of lead in drinking water. Other sources of lead in water include emission from leaded fuels as well as lead paints. Lower levels of lead are found in fertilizers (Mortvedt, 1995).

Lead gains access into the human body via water we drink, food and air (inhalation). Accumulation of lead inside of the human body system is toxic to infants, children, fetus and pregnant women since it affects the human's central nervous system. Lead also affects the optimum functioning of major enzymes that take part in the biosynthesis of harem. Other effects of lead include dullness, irritability, poor concentration, restlessness and damage to the kidney, among other effects. WHO sets a guideline value for lead content in water that is drinkable to be 0.01 mg/L (WHO, 2006). Lead exerts specific toxic effect on fish blood and tissues when it enters aquatic system (Mousa & Khattab, 2003). It is also a known cause of neurological disorder which arises during fetal development (Goyer & Clarkson, 2001). Domestic water discharge and fertilizers may be causing lead pollution at the tributaries and there no documentation on lead levels at these tributaries. Laboratory analysis of the existence of lead in water includes anodic stripping voltammetry and atomic absorption spectrometry (WHO, 2012).

2.4.3.5 Chromium (Cr)

The main entries of chromium into surface water are through sewer sludge, cement works and municipal waste (ARB, 1986). This is found in the earth's crust and widely spread inside soils and rocks. Chromium ionizes to form chromium (III) ions (Cr^{3+}) and chromium (VI) ions (Cr^{6+}) and

are the most stable oxidation states of chromium that takes part in chemical reactions. Cr^{6+} is a byproduct of industrial applications and textiles. Chromium has a molecular mass of 52g/mol.

Intake of chromium in negligible quantities does not pose any risk to human health. An intake of 50 – 200 $\mu\text{g Cr}^{3+}$ daily is essential for normal glucose, protein and fat metabolism in human beings (ATSDR, 2003). Consumption of very high doses of chromium ion of between 1-5g per kilogram of body weight may cause acute health risks, including death. The USEPA has classified Cr^{6+} as a human carcinogen and the most toxic, though the body is able to reduce it to Cr^{3+} which is less harmful, but it readily damages cell walls being a strong oxidizer. It also prevents growth in algae and duckweed lowers survival of benthic invertebrates and reduces growth of freshwater fingerlings” (USEPA, 1994b). The compounds of Chromium as well as Chromium itself, are used to manufacture catalysts, in leather tanning industries, ceramic and glass industries, fungicides, pigments and paints among other uses.

WHO (2006) guideline value for the presence of total chromium (Cr^{6+}) in drinking water is 0.05 mg/L. The possible chromium pollution at these tributaries are sewer sludge, cement works and general municipal waste getting into the rivers at the urban centers. The level of chromium in in Ndakaini dam is not known.

2.4.3.6 Copper (Cu)

Copper commonly gets into to the water systems through agricultural activities such as application of fungicides, sewage, vegetation, wood production and phosphate fertilizer application (Dameron & Howe, 1998; USEPA, 2007). At low concentrations, Copper is essential micronutrient in humans and other vertebrates. Copper assists in the electron transfer process in humans, which also involves iron in hemoglobin, photosynthesis in plants, and the last phase of mitochondrial respiration; hence, copper regulates life support processes such as red blood cell creation and glucose synthesis (USEPA, 1980). In plants, it has been used to control algal growth in water bodies, however, when inappropriately applied becomes toxic to fish, invertebrates and amphibians (Horne & Dunson, 1995). At the same time, at high concentrations copper affects root growth and morphology in plants. This is due to accumulation of copper in root tissue with little of it being translocated to the shoots (Marschner, 1995). In humans it causes Menke’s disease and Wilson’s disease, which is a genetic disorders associated with accumulation of copper in vital organs in the body such as kidney, liver and brain (Prasad & Oberleas, 1976). The application of

fertilizers and fungicides in farming and also domestic waste water are possible copper pollutants at the tributaries, and the copper levels at these tributaries have not been established. Results from several researches coming from Canada, Europe, and the USA suggest that copper levels in drinking-water ranges 0.005 to >30 mg/litre, with the predominant source being inner copper pipe corrosion. (US EPA, 1991; US NRC, 2000). According to WHO (2008 & 2011), copper has a guideline value of 2 mg/l adopted by WHO since 1993.

2.4.3.7 Iron

Iron is one of heavy metals which are considered useful in the human body and it is present in nearly every food with higher concentrations in animal tissues than in plants (Engwa *et al.*, 2019). Iron is the major component in blood formation and a constituent of hemoglobin that takes part in many physiological activities. Iron deficiency is the most common cause of anemia and according to Engwa *et al.*, (2019). Mental disorders and reduced intellectual performance in animals and children have been observed to be closely associated to iron deficiency. Therefore, iron contributes significantly to brain development (Agarwal, 1990). Iron in a free state can generate hydroxyl radicals which are capable of interfering with biological molecules like lipids, proteins, and even DNA. The exposure routes of Iron salts are oral, dermal and inhalation (Engwa *et al.*, 2019).

The toxicity of iron salts (iron sulfate monohydrate, iron sulfate, and iron sulfate heptahydrate) depends on the route, amount, and period of exposure. Some acute health effects associated with exposure to iron metal include diarrhea, vomiting, and gastrointestinal bleeding. Chronic health impacts of long-time exposure to iron metal include tachycardia, shocks, metabolic acidosis, lethargy, cancer, etc. (Engwa *et al.*, 2019). Excess iron in aquatic systems can damage fish by blocking gills and lowering respiratory potential and consequent survival," according to the study (Peuranen *et al.*, 1994). Subsequently, high iron concentrations can cause reduction in species diversity of benthic invertebrates and fish. Iron may be getting into the tributaries through organic waste discharged from households. The permissible consumption limit of iron by WHO is 0.1 mg/l (Paul, 2017).

2.4.4 Biological Parameters

Water is regarded to be the most important necessity for human and industrial progress. The demand for freshwater has increased in recent decades due to industrialization and growth of population. The supply of water for agriculture and human life is compensated by the rivers. As a

result of industrial effluents and other sources from anthropogenic activities sources of contamination into the rivers, the water quality gets demerited hence threatening the human and aquatic life. Assessment of water quality can be ascertained by the presence or absence of microorganisms which act as indicators. These indicator organisms are very vital components of micro biological testing programs done by the food industry and other regulatory agencies. The indicators are thought to imply the probable presence of pathogens. Microbes contained in the wastewater are thought to transmit disease, therefore microbial water quality assessment and sanitary inspection best describes the quality of water consumed (Paruch *et al.*, 2019).

2.4.4.1 Total Coliforms

Coliforms are a vast group of various kinds of bacteria which are gram negative, able to grow in presence of bile salts and can ferment lactose to produce gas and acid in a life span of 48 hours at a temperature of 37 degrees Celsius (Tortorello, 2003). Coliforms testing have been recommended since 1900s for testing water quality. According to the National primary drinking water regulatory, there should be a continuous monitoring of water used for drinking for the presence of fecal coliforms which signify positive testing of *E. coli*.

Fecal coliforms, also known as thermotrophic, thermoduric, or thermotolerant coliforms, have the same characteristics as the coliform group, except that fermentation may take place at 44.5-45.5 °C (Tortorello, 2003).

2.4.4.2 E-Coli

Aquatic microbiota contributes very largely to the sustainability of the natural ecosystem. However, it can threaten the life of animals and humans by carrying pathogens which cause water-borne diseases. Total coliform is a vast group of various kinds of bacteria. Total coliform, *E. coli*, and fecal coliform can be used to determine drinking water quality. Fecal pollution of water can cause the introduction of pathogens into the gastrointestinal tract of mammals. It can be determined by fecal indicator bacteria (*Escherichia coli*, *E. faecalis* and *E. faecium*).

Higher densities of fecal coliforms are recorded in sediments than in water (An *et al.*, 2002). Some of the sources of *E.coli* pollution in surface water include: Septic leachate, Wildlife populations, Storm and agricultural runoff, Municipal wastewater, Non-point sources of animal and human waste.

Pollution of water bodies is thought to transmit pathogenic diseases like typhoid and cholera. These pathogenic organisms enter the gastrointestinal tract through ingestion or infection of the nasal cavity, skin, ears, and eyes. Some of the health effects associated with fecal pollution include vomiting, diarrhea, anemia, hepatitis, amoebic dysentery, and respiratory diseases (Opisa *et al.*, 2012).

2.5 Sedimentation in Water

Chabukdhara & Nema (2012) surmised that there is widespread worry about heavy metal pollution due to their environmental durability, biogeochemical recycling, and the ecological dangers that metals provide. Yi *et al.*, (2011) noted that many human activities created heavy metals from metropolitan areas, agricultural regions, and industrial sites and discharged into aquatic habitats, where they are carried in the water column, stored in sediment, and biomagnified through the food chain. This results in substantial ecological risk to benthonic organisms, fish and humans according to Uluturhan, & Kucuksezgin (2007).

Sediments in water bodies form an important habitat for aquatic organisms. At the same time they act as natural source and sink for various substances including nutrients and heavy metals (Biney *et al.*, 1994). Therefore, the quality or quantity of sediments or even both exert an impact on ecological quality (Stronkhorst *et al.*, 2004). The sediments, both suspended and precipitated substances deposited on the bottom of the water, constitute a reservoir for many pollutants and trace substances (Biney *et al.*, 1994; Barbour *et al.*, 1999). These pollutants are slowly released into overlying surface water hence altering water quality downstream.

2.6 Relationship of Water Quality and Rainfall Variations

Rivers are exposed to a number of natural processes occurring in the environment, including the hydrological cycle. Rainfall variations affect the flow rate of water downstream, substance input and transport, and sedimentation leading to changes in physicochemical parameters. Baird and Ulanowicz (1989) therefore, noted that seasonal trends in nutrient concentrations and distributions have therefore been identified. For instance, nitrates are known to accumulate during dry seasons, and large amounts of nitrates are only observed during early wet seasons. Because early rains wash off deposited nitrate from near-surface soils, nitrate levels drop dramatically as the rainy season develops (Wolfhard & Reinhard, 1998). This aspect is considered as the "solution effect", in which salt from dead animals and vegetation on dry land penetrate into the waters during heavy

downpour. This also causes an increase in mineral content and electrical conductivity of the water in a river. However, there is also the "dilution effect" in which different mineral concentrations present in the water, decrease during the wet season (Eduardo *et al.*, 2020).

Similarly, water temperature decreases during rainy season due to a reduction in air temperature. Rainfall seasons in the Mara River Basin are variable, however, there is a lengthy wet season from March to June and a short-wet season from September to December. Though the volume of water varies from year to year, the Mau area receives 1,000 to 1,750 mm of yearly rainfall (Mati 2005). The quantities of agriculturally related materials such as unutilized fertilizers and livestock waste, and domestic wastes from households getting their way into the water downstream may be subject to seasonal cycles. There is limited documentation indicating the variations in physicochemical parameters of water and sediments related to the different rainfall regimes along Ndakaini dam.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Description of Study Area

This study was carried out in Ndakaini Dam which is located at the upper Thika basin in Gatanga Sub County, Murang'a County, at 0° 49' 13" S, 36° 51' 1" E (-0.820278, 36.850278) with an altitude of 1800 meters above sea level. It was formerly called Thika dam because it is principally fed by Thika River but subsequently adopted the name Ndakaini dam to reflect the location where the dam is situated.

It has a water holding capacity of 75million cubic meters and supplies about 85% of its total volume of water to Nairobi County. The safety and quality of water flowing in and out of Ndakaini Dam are essential because it is depended mainly on for water supply to over 4.6 million people living in the city of Nairobi (KNBS, 2019) and also Gatanga environs.

The three primary rivers that drain their water directly into the Dam are river Thika, river Githika and river Kayuyu with Thika River contributing 50% of the Dam's water (Oates & Marani, 2017). River Githika and river Kayuyu drain 30% and 20% of the Dam's water respectively.

The upper Thika basin receives two significant rainfall seasons called the bimodal rainfall pattern that occurs in March-May and in October – December annually due to the Inter-Tropical Convergence Zone (ITCZ). Additionally, the Dam is also fed with water from orographic rainfall, which refers to rainfall that results from moist air rising over a mountain. Ndakaini Dam's orographic rainfall results from the rising wind over Aberdare range consisting of Gatare and Kimakia forests (University of Nairobi, 2019), thereby contributing to a total annual rainfall of between 2000 mm and 2500 mm.

The human activities that go on upstream of the dam include agricultural activities like large scale growing of tea and Napier grass. Located also in the downstream of the dam are farm lands of food crops such as cabbages, potatoes, maize also spinach and kale vegetables. Napier grass and fruit trees are also grown. Dairy farming, eucalyptus tree felling are some of the activities observed in Ndakaini water catchment area. Also, lack of domestic waste treatment plants at both Thika and Muranga trading centers was also observed throughout the study period. Most of these crops are

pesticide dependent for their growth survival. The sources of pollution to Ndakaini Dam include agricultural practices, domestic and industrial wastes (Macharia, 2015).

3.1.1 Features of the Dam

Ndakaini Dam was constructed between the year 1989 and 1994 by Strabag International as the main contractor and Howard Humphreys (K) Ltd as the Consultant Engineers. The estimated cost of the project was two billion Kenya shillings, funding which was mainly done by the World Bank, European Investment Bank, ADB, as well as the Kenyan Government (University of Nairobi, 2019). The location of the Dam within the region was decided on due to the incised deep valley of upper Thika River, among other reasons. Ndakaini Dam has an embankment height of sixty-five Metres (65m) and a capacity to contain a total of 70 million cubic metres (70M m³) when full (Olima & K'kakumu, 1999). In summary, the significant features of the Dam are as shown in table 3.1 below.

Table 3.1: Significant features of Ndakaini Dam

Dam Component	Characteristics
Height of Dam	65m
Storage capacity	70,000,000m ³
Reservoir water surface	2.8km ²
Catchment area	75 km ²
The full water supply level	2041 AOD
Dam Crest length	420 m
Spillway shaft diameter	5.5m
Spillway design capacity	559m ³ /sec
Tunnel length	340m
Tunnel	Discharge: 390m ³ /s, length: 180m
Emergency spillway	Qmax = 120m ³ /s

Source: *Nairobi Master Plan Report (2011)*

3.2 Sampling Sites

Nine sampling sites were mapped for sample collection; that is on the surface of the dam and on seven different inlet and outlet rivers. On the surface of the dam, water was collected at the middle, left and right of the dam. Thika, Kayuyu and Githika River were sampled as the inlets while Kiama, Gituru and Chania outfall as the outlets of the dam. The seven sampling stations selected were representative sampling stations covering both the upstream, downstream and the dam sections in

the study respectively. The map in figure 3.1 shows the sampling sites indicated in purple coloured dots while table 3.2 details the location and coordinate of each sample point.

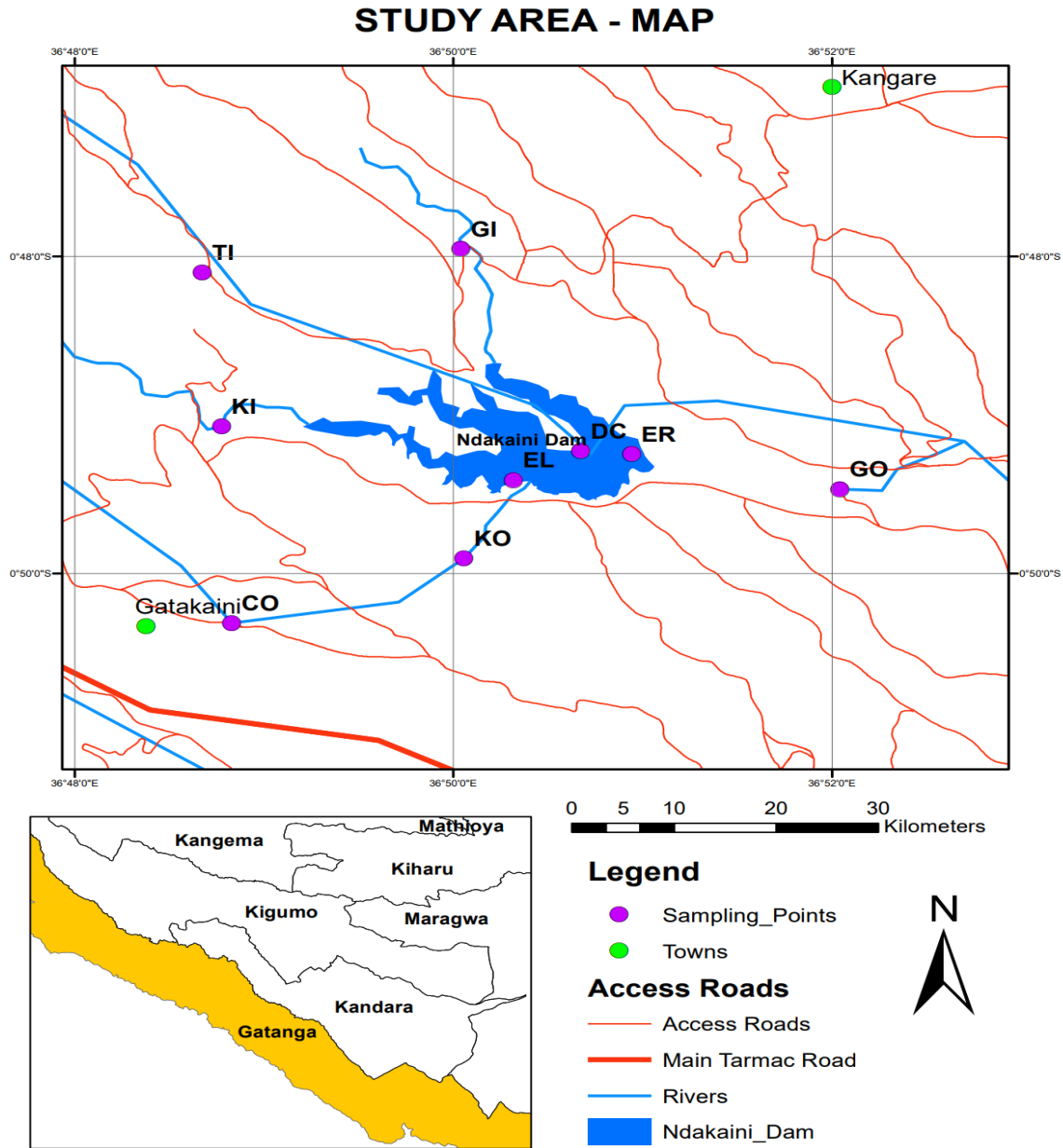


Figure 3.1: Map of Ndakaini Dam, Study Site (Source: GIS LAB, 2019)

Table 3.2 Sampling Sites and Gps Coordinates

Site No.	Sampling Sites Name	Site Codes	Gps Coordinates	Site Location and Description
1.	Thika inlet	TI	-0.8244684, 36.8673701	This site is 100 metres from the dam location and located in Wanyanga. The main agricultural activities of this catchment is maize and cabbage farming.
2.	Githika inlet	GI	-0.799194, 36.834028 -0.824468,36.867370	This site is near Bakomboki Tea factory and is 500m from the dam location. This river is full of silt and gravel. The agricultural activities around this site is tea farming and Napia grass plantation.
3.	Kayuyu inlet	KI	-0.807787, 36.812657	This site is located at Kimandi area and the downstream of the river. There is a lot of Eucalyptus trees and shrubs nears the river. This site is 200 metres from the dam location.
4.	Kiama Outlet	KO	-0.831734, 36.8342902	This is direct outlet from the dam down to Chania River, 1 kilometre from the location of dam and has quite a lot of algae.
5.	Gituru Outlet	GO	-0.824472, 36.867361 -0.824468, 36.867370	A site for water compensation to communities downstream. The surrounding near the river is muddy with a lot animal dung around. This indicates a lot of animal rearing observed around this site, hence this site is a source of drinking water to the animals like cattle, cow. It is 2 kilometres from the dam location and near Gituru shopping centre.
6.	Chania Outlet	CO		This sampling site is 7 Kilometres from the dam itself and is located in

			-0.843288, 36.8114672	Kiarutara. The water from the dam meets at Kiama river which finally discharges at Nyetu treatment works.
7.	Dam Centre	C	-0.822608,36.646342	This is middle part of the lake with little or no anthropogenic/human activities
8.	Edge left	E _L	-0.824753, 36.850975	This is the left hand side part of the dam on entering the dam.
9.	Edge Right	E _R	-0.820055, 36.847179	This is the right-hand side part of the dam on entering the dam.

3.3 Collection and Preservation of Sample

Water samples were collected in accordance to the method described by Ozturk *et al.*, (2009). This is an US EPA method for collection and analysis of surface water samples. Both sediment and water sampling were done over two seasons, dry season and wet season. The dry season sample collection was carried out on September, 2020 while in the wet season, sample collection was carried out on April, 2021.

Water samples were collected in triplicates from all nine sampling sites into 1 litre polyethylene bottles that were pre-sterilized with dilute aqua regia and rinsed very well with large quantities of deionized water. Specific precautions were taken to minimize contamination. In order to provide a representative sample, before immersing the sampling bottles to about 10 cm below the surface of the water using grab method, the bottles were rinsed thrice with the surface water from the sampling site. Water samples for heavy metal analysis were acidified with 5mls of HNO₃.

Three Sediment samples were collected from site KI, GI and GO using pre-cleaned stainless steel shovel and packed into ziplock bags as shown in figure 3.2. Both the bottles and ziplock bags were labelled accordingly and stored in polyurethane cooler boxes stocked with ice packs and transported to the University of Nairobi, Department of Chemistry laboratory where water samples were stored in a refrigerator at 4⁰C while sediment samples stored in the freezer at -2⁰C respectively, prior to analysis.

The physio-chemical parameters like turbidity, pH, temperature and electrical conductivity were determined in situ using their respective well calibrated meteres while DO and TDS was

determined within 5 hours of sample collection in the laboratory. Analysis of other water sample parameters were carried out within one week at Government Chemist laboratory and in Pesticide Research Laboratory at Department of Chemistry, University of Nairobi within 5 hours of sample collection in the laboratory.



Figure 3.2: Sediment collection from site GO

3.4 Laboratory Equipment, Reagents and Apparatus

The equipment used were calibrated to ensure their optimum performance. During the laboratory analysis, chemicals and reagents used were of analytical grade. Validation of the method and regular analysis of the blank solution was done. Also, clean glassware soaked in 10% HNO_3 (v/v) was used to ensure no cross-contamination of samples occurred (Mwamburi, 2009), thereafter were rinsed thrice with deionized water and dried in oven.

3.4.1 Chemicals and Reagents

The chemicals and reagents used for water analysis were acetylene standard (analytical grade), conc. sulphuric acid (H_2SO_4), 0.25N potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), silver and mercuric

sulphate, standard buffers (pH 4,7 and 10), ferrous ammonium sulphate (FAS), ascorbic acid, distilled and deionized water, perchloric and nitric acid, 1,10-phenanthroline and starch indicator, sodium thiosulphate and potassium iodide.

3.4.2 Glasswares and Apparatus

Sample bottles and ziplock, volumetric flasks (1000ml), Erlenmeyer / conical flasks (500ml), graduated measuring cylinders (500ml), pipettes, vials, beakers, burette, round-bottomed flasks, retort stand and clamps, glass beads, aluminum foils, Whatman filter papers (0.45 μ m), shovel, cooler boxes and ice packs.

3.4.3 Instruments

Portable pH, TDS multipara meter (Hanna model: HI 9812-5), analytical balance accuracy of 0.001g, water deionizer (model: Evo-CB Dio VFT –M), thermometer electrode (Hanna model: HI 9125), computer, drying oven (Daihan model:FHX-05), UV-vis spectrometer, hot plate, reflux apparatus, atomic absorption spectrophotometer (Analytik jena, model contra 700)

3.5 Laboratory Analysis of Samples

The tests and analysis of the samples were conducted adhering to the standard methods recommended for the examination of water quality and wastewater.

3.5.1 Determination of Heavy Metals

3.5.1.1 Acid Digestion of Samples for Heavy Metal Analysis

Digestion of acid blanks, water and sediment samples was done following USEPA Method 3005A. The sediment were defrosted so as to bring them to room temperature. Sediment samples were oven-dried at 105°C, sieved (<2 mm) and then ground using mortar and pestle. Thereafter, 1 g triplicate ground sediment samples were weighed and transferred into a pre-cleaned 250ml beaker containing 10 ml of 10% aqua regia and 1ml of analytical grade perchloric acid. The beaker containing the sample was digested at 90°C for 45 minutes. After total digestion and subsequent cooling, the remaining sample solutions after evaporation were filtered using Whatman filter paper and then transferred to a 250 ml volumetric flask and topped up to the volume using distilled water. Acid blanks followed the same procedure for digestion using de-ionized water but without the addition of water samples.

For water samples, 100 ml aliquot of well mixed samples in triplicate were digested following the aqua regia and perchloric acid method above and thereafter reconstituted to final volume of 100 ml. For quality control for both water and sediments, acid blanks were subjected to the same digestion procedures above. The extracts were analyzed for Mn, Cd, Cr, Zn, Cu, Fe and Pb using an Atomic Absorption Spectrophotometer.

3.5.1.2 Preparation of Heavy Metal Standard Stock Solution and Calibration Standards

To obtain a calibration curve, AAS instrument followed preparation of series of standard solutions of known concentrations from standard stock solutions. Standard stock solutions of the specific heavy metal ions of Lead (Pb), Cadmium (Cd) Chromium (Cr), Iron(Fe), Zinc (Zn), Manganese (Mn), and Copper (Cu) at a concentration of 1000ppm; traceable to NIST were diluted to give five calibration standard solutions in the range 0.001 to 5ppm. Standard preparation were done manually whereby concentrations 100 ppm, 10ppm, 1ppm of each metal were prepared from a 1000ppm stock solution following dilution formula of $C_1V_1 = C_2V_2$ where

- C_1 = Initial concentration of solution
- V_1 = Initial volume of solution
- C_2 = Final concentration of solution
- V_2 = Final volume of solution

3.5.1.3 AAS Analysis of Samples for Heavy Metals

After digestion of the water and sediment samples, analysis using Atomic Absorption Spectrometer (Analytik Jena, model contra 700) was employed for assessment of some selected heavy metals: Mn, Cd, Cr, Zn, Cu, Fe and Pb. Five calibration standards were prepared for each heavy metal under study. Each metal was analyzed using a specific hollow cathode lamp for each metal. 1.0 mL of digested samples were aspirated into the flame and atomized and distilled water used to auto zero. A light beam was directed through the flame into monochromator and onto a detector which measured the amount of light absorbed by the atomized element in the flame. Each metal has got its own unique absorption wavelength and a flame/gas as shown in Table 3.3. Also a source lamp composed of the elements was used, this made the method relatively free from spectral or radiation interference.

Table 3.3: Limits of detection and wavelengths for analyzed elements

Element	Wavelength (nm)	Flame / gases	Limit of detection (mg/L)
Cd	228.6	Air/acetylene	0.001
Cu	324.7	Air/acetylene	0.002
Pb	217	Air/acetylene	0.001
Cr	359	Air/acetylene	0.005
Zn	213	Air/acetylene	0.01
Fe	248.1	Air/acetylene	0.0018
Mn	279	Air/acetylene	0.0001

Source: Government Chemist Nairobi Operator Result Sheet.

After analysis, the concentration of elements were determined from the calibration graphs of concentrations of the standards against the absorbance generated by the instrument. The calibration standard data and curve for Mn, Cd, Cr, Zn, Cu, Fe and Pb are given in the appendices 1-8.

Determination of Silicon (Si) element was analyzed only for water samples in dry and wet season using a Uv-Vis spectrophotometer (Hach Model: DR 8000).

3.5.2 Determination of Physiochemical Parameters

3.5.2.1 pH

Measurement of pH of water samples were determined in-situ using calibrated portable, multiparameter (Hanna model: HI 9812-5). Calibration of the meter was carried out using buffer solutions (pH 4, 7 and 10) for pH measurements. The pH electrode was dipped directly into the sample solution, swirling and waiting for steady reading. The electrodes were thoroughly rinsed with distilled water and then carefully wiped with a tissue paper before changing into another sample and after use. All readings were taken in triplicate and recorded.

3.5.2.2 Electrical Conductivity

Electrical conductivity testing of the water samples was carried out using calibrated portable, multipara meter (Hanna model: HI 9812-5). Calibration of the conductivity meter was performed to obtain optimum efficiency using 84 us/cm, 1413us/cm and 12880 us/cm standards respectively.

3.5.2.3 TDS

TDS measurement was carried in-situ as well using calibrated portable, multipara meter (Hanna model: HI 9812-5) and also calibration for TDS measurements were performed to ensure accuracy of readings.

3.5.2.4 Temperature

Water temperature measurements were made in degrees Celsius units, using a digital thermometer probe (Hanna model: HI 9125) by directly dipping the thermometer into the surface water at sampling sites under study. The temperature was read and reported to 1 decimal place. All readings were observed and compared with the KEBS and WHO, potable water standards.

3.5.2.5 Dissolved Oxygen and Odour

Well calibrated Hach Luminescent DO sensor probe was used in taking the readings of dissolved oxygen for water samples respectively while odour was assessed using organoleptic threshold odour number (TON).

3.5.2.6 Colour

Analysis of colour in water samples were carried out using platinum-cobalt standard method (APHA) using a spectrophotometer (Hach model: Dr 5000) and read at LR 465nm. Firstly, the blank was prepared by filling the sample cell with 10ml of filtered deionized water, followed by filling a second sample cell with 10ml of filtered sample. The blank was inserted into the cell holder, pushed to zero button to display zero (0) units pt-co followed by inserting the prepared sample into the cell holder and results read in pt-co units.

3.5.2.7 Turbidity

Determination of turbidity for water samples was carried out using a turbidimeter by Nephelometry method (USEPA: 180.1). Formazin; a primary stock standard suspension (20,100,800 NTU) was used to calibrate the instrument prior to analysis.

3.5.2.8 Total Suspended Solid (TSS)

TSS of water samples were determined spectrophotometrically using UV-vis instrument (Hach Model: Dr 5000) and readings obtained at 810 nm.

TSS is measured gravimetrically. 100ml of the water sample is weighed and filtered through a glass micro fiber filter paper which has been previously dried at 105 °C and weighed. The residue on the filter is completely rinsed with distilled water, dried in an oven at 103 to 105 degrees Celsius for 1 hour, and then chilled in a desiccator until the weight of the filter does not change. The weight difference represents the total weight of the suspended particles. The total suspended particles are represented by the increase in filter weight. TSS can alternatively be calculated by calculating total solids and removing total dissolved solids. The kind of filter holder, porosity, area, pore size, and thickness of the filter, as well as the physical nature and particle size, all have an impact on the separation of suspended particles from dissolved solids and the amount of material deposited on the filter. TSS is measured in milligrams of sample per litre (mg/L) (APHA, 1998).

3.5.2.9 Total Hardness

Reagents

(a) Buffer solution

40g of borax was dissolved in 800ml water. 10 g NaOH and 5g sodium sulphide was dissolved in 100ml water. These two solutions were allowed to cool and then mixed together and diluted to 1 litre (1000ml).

(b) Standard Calcium Chloride Solution:

1g of pure CaCO₃ was dissolved in 50ml water in a conical flask. 20.5 ml normal HCl was cautiously added, warmed, allowed to cool down and then transferred to 1litre flask and topped up to mark. 1ml =1mg CaCO₃.

(c) N/50 EDTA:

4g EDTA was dissolved in 800ml water. 21.5 ml of N/1 NaOH and 0.1g magnesium chloride was added and titrated against standard calcium chloride solution. The solution was adjusted so that 1ml EDTA = 1mg Ca as CaCO₃.

(d) Pdf Total Hardness Indicator

Procedure

Water samples for total hardness analysis was carried out using EDTA Titration Method. 20 ml of water sample for was pipetted into a small porcelain dish. Half tablet of total hardness indicator was crushed into the dish containing the water sample and 1 ml buffer added as well, then the solution turned wine-red in colour. The solution was titrated against N/50 EDTA, when the Ca and Mg ions are complexed at the end point, there was a colour change from wine –red to light blue colour.

Calculation

$$\text{Total hardness} = \frac{\text{ml of EDTA Titre} \times 1000}{\text{Volume sample taken}} \quad \text{mg/l / ppm}$$

3.5.2.10 Calcium Hardness

Reagents

(a) 1N Sodium Hydroxide as buffer.

(b) Calcium Chloride Solution:

1g of pure CaCO₃ was dissolved in 50ml water in a conical flask. 20.5ml normal Hcl was cautiously added, warmed, allowed to cool down and then transferred to 1litre flask and topped up to mark. 1ml =1mg CaCO₃.

(c) N/50 Ca²⁺ EDTA:

4g EDTA was dissolved in 800ml water. 21.5 ml of N/1 NaOH was added and titrated against standard calcium chloride solution. The solution was adjusted so that 1ml EDTA = 1mg Ca as CaCO₃.

(d) RDH Calcium hydroxide Indicator (Briochrome blue-black R)

Procedure

Water samples for calcium hardness analysis was carried out using EDTA Titration Method. 20ml of water sample was pipetted into a small porcelain dish. Half tablet of calcium hardness indicator was crushed into the dish containing the water sample and 1 ml NaOH buffer added as well. Then, the solution was titrated against N/50 EDTA until there was a colour change to Violet.

Calculation

$$\text{Calcium as CaCO}_3 = \frac{\text{ml of EDTA Titre} \times 1000}{\text{Volume sample taken}} \quad \text{mg/l / ppm}$$

Converting CaCO₃ to elemental Ca, that is converting mg of CaCO₃ per litre to mg Calcium per litre

$$= \frac{\text{ml of EDTA Titre} \times 1000}{\text{Volume sample taken}} \times 0.4$$

3.5.2.11 Total Alkalinity

The alkalinity of both natural and treated waters is typically caused by the presence of carbonate, bicarbonate, and hydroxide compounds of Ca, Mg, Na, and K. In natural waters, the alkalinity is usually due to Ca (HCO₃)₂.

Reagents

- (a) N/50 Hydrochloric acid prepared from N/1 HCl previously prepared from an ampoule.
- (b) Phenolphthalein indicator (as for acidity)

(c) N/10 sodium carbonate, for standardizing hydrochloric. 5.3 g of anhydrous sodium carbonate dried at 250°C was dissolved in water and marked up to 1 litre.

Procedure

Water samples were analyzed for total alkalinity by titration method where phenolphthalein result values were subtracted from methyl orange result values. 20 ml of water sample was pipetted into a small porcelain dish. Three drops of Phenolphthalein was added to the water sample in a bowl and titrated against 0.02N of HCl, there was no colour change as the pH of water samples were not above 8. This is known as phenolphthalein alkalinity.

On addition of three (3) drops of methyl orange to the water samples, there was a colour change to orange and after titration, colour changed to light pink. Burette reading was recorded. This alkalinity is referred to as total alkalinity.

3.5.2.12 Silicon

Silicon as silica in water samples were determined by silicomolybdate method 8185 using a spectrophotometer (Hach model: Dr 5000) and read at HR 452 nm. This method involves using high range silica reagent set. Firstly, the program was started at 656 Silica HR, followed by filling a sample cell with 10ml of water sample and then adding the contents of one Molybdate reagent powder pillow for high range silica to the cell, swirled until the reagent is completely dissolved. Another contents of one acid reagent powder pillow for high range silica was added to the cell swirled and waited for 10 mins to completely react. The colour of the water sample turned yellow. When the 10 minutes timer expired, the contents of one citric acid powder pillow was added to the sample cell and waited for 2 minutes reaction time to occur. After 2 minutes timer expired, the blank sample was inserted into the cell holder and pushed to zero, the display showed 0 mg/L SiO₂ followed by inserting the prepared water sample into the cell holder and results read in mg/L SiO₂.

3.5.3 Determination of Nutrient Parameters

3.5.3.1 Fluoride

Colorimetric determination of fluoride for water samples were carried out using alizarin complexation method.

Reagents

(a) **Fluoride Standard Solution:** 0.221 g of NaF was dissolved in water and topped up to 1 litre mark. (1ml = 0.1mg of Fluoride).

(b) **Acid Zirconium-alizarin Solution:**

- **Solution A** 0.7 g of alizarin red S (sodium alizarin sulphate) was dissolved in 100 ml water.
- **Solution B** 0.45 g zirconium chloride dissolved in 100 ml water.
- **Solution C** 70 ml conc. H₂SO₄ was carefully added to 700 ml of water (H₂O) and was allowed to cool. To prepare the reagent, solution A was poured into solution B and the mixture then added to solution C and diluted to 1 litre. The solution was stored in the dark and used within 24hrs of preparation.

Procedure

The water samples was put in a 50 ml Nessler tubes / cylinders. Fluoride standards was prepared. As shown in figure 3.3, appropriate volumes of fluoride standard solutions was pipetted into similar Nessler tubes in the range of 0.1 ml, 0.2ml, 0.3, 0.4 and 0.5ml respectively and topped up to 50 ml mark. (0.1ml of fluoride solution = 0.01mgF⁻¹). 50 ml of distilled water not containing the fluoride standard solution was used as blank. Thereafter, 1ml of zirconium-alizarin solution was pipetted into each Nessler tubes containing water samples and waited for 5 minutes. Accompanied colour changes were compared across the tubes and readings recorded.



Figure 3.3: Fluoride samples analysis (Alizarin method)

3.5.3.2 Chloride

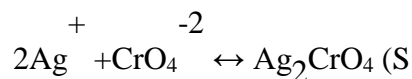
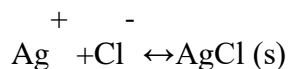
Determination of chloride in water samples utilized Mohr's method (USEPA method 9253) using silver nitrate (AgNO_3) as titrant and potassium dichromate as an indicator.

Reagents

- (a) **AgNO_3 solution (0.0282 N):** 4.791 g of AgNO_3 dried at 105°C was weighed and dissolved in distilled water and marked up to 1000ml.
- (b) **Sodium Chloride Standard Solution:** 0.1649 g of pure sodium chloride, dried at 105°C was dissolved in distilled water and marked up to 1000ml.
- (c) **Potassium Chromate indicator solution:** 5g of potassium chromate was weighed and dissolved in a beaker containing distilled water and marked up to 100 ml. A few drops of silver nitrate solution were added until a faint crimson precipitate formed. After 12 hours, the solution was filtered through filter paper and the filtrate was diluted to 1 Liter with distilled water.

Procedure:

The burette was thoroughly rinsed and filled with silver nitrate solution. Then, 20 ml of water sample was poured into the porcelain dish and 1 ml of 5% Potassium dichromate (K_2CrO_4) added as indicator solution to get a yellow colour and then titrated with 0.0282N of Silver nitrate (AgNO_3) until the slightest reddish colour due to the excess formation of silver chromate appears (end point). Colour changed to red marks the completion of the experiment. Readings were recorded and data was transcribed for analysis.



There was also blank titration whereby 20 mL of the distilled water was added to porcelain dish, on addition of 1 mL of potassium chromate indicator to the dish, light yellow colour was achieved. The sample was titrated against silver nitrate solution until the colour changed from yellow to brick red as well. The volume of silver nitrate added for distilled water was noted.

3.5.3.3 Nitrates

Nitrates in water samples was determined by UV-vis spectrophotometer (Hach model Dr 5000) Nitrate Low Range (LR), Hach method 8039 (also known as Cadmium Reduction method) using powder pillows.

Procedure:

10mls of water sample was pipetted into cuvette (sample cell) followed by addition of contents of NitraVer 5 reagent powder pillow to the sample cell and shaken thoroughly for 1 minute to dissolve powder and 5 minutes wait reaction to occur. An amber colour shows presence of nitrite in the water sample. When the timer expired, the UV-Vis was blanked with deionized water and pushed to zero then followed reading of the prepared water samples. Nitrate test results was measured (read) at a wavelength 500 nm and reported in mg/L NO₃ —N.

3.5.3.4 Nitrites

Nitrites in water samples was determined by UV-vis spectrophotometer (Hach model Dr 5000) by 371 Nitrite Low Range (LR) method 8507 using powder pillows. This is USEPA Diazotization method for water, wastewater and seawater application.

Procedure:

10 mls of water sample was pipetted into cuvette (sample cell) followed by addition of contents of NitriVer 3 reagent powder pillow to the sample cell and shaken thoroughly for 1 minute to dissolve powder and 20 minutes wait reaction to occur. A pink colour shows if there is nitrite in the water sample. When the timer expired, the UV-Vis was blanked with deionized water and pushed to zero then followed reading of the prepared water samples. Nitrite test results was measured (read) at a wavelength 807 nm.

Principle:

When nitrite interacts with sulfanilic acid in the sample, it produces an intermediate called diazonium salt. This salt combines with chromotropic acid to generate a pink complex that is proportionate to the amount of nitrite present.

3.5.3.5 Sulphate

In this study, sulphate in water samples was determined by UV-vis spectrophotometer (Hach model Dr 5000) method 8051 using powder pillows. The procedure is equivalent to USEPA method 375.4 for wastewater.

Procedure:

10mls of water sample was pipetted into cuvette (sample cell) followed by addition of contents of SulfaVer 4 reagent powder pillow to the sample cell and then shaken thoroughly for 1 minute to dissolve powder and 5 minutes wait reaction to occur. The Hach pillow powder reagent contains BaCl_2 , dihydrate (40 - 50 %) and citric acid (50 – 60%). White turbidity will form if sulphate is present. Sulphate ions in the water sample reacts with barium in the Sulfaver 4 and form a precipitate of barium sulphate. The amount of turbidity formed is proportional to the sulphate concentration. When the timer expired, the UV-Vis was blanked with deionized water and pushed to zero then followed reading of the prepared water samples. Sulphate test results were measured (read) at 450 nm.

3.5.3.6 Phosphate

Phosphate in water samples was determined by UV-vis spectrophotometer (Hach model Dr 5000) ascorbic method 8048 using powder pillows. This method is also known as phosphorus, Reactive (Orthophosphate). The procedure is similar to USEPA and standard method 4500-P-E for wastewater and an acceptable version of EPA method 3651, adapted from Standard Methods for the Examination of Water and Wastewater.

Procedure:

10mls of water sample was pipetted into cuvette (sample cell) followed by addition of contents of PhosVer 3 Phosphate reagent powder pillow to the sample cell and shaken thoroughly for 1 minute to dissolve powder and 2 minutes wait reaction to occur. The Hach pillow powder reagent contains Potassium Pyrosulphate, L-Ascorbic Acid, Sodium Molybdate, Tetrasodium EDTA and Dihydrate. Sulphate ions in the water sample reacts with barium in the Sulfaver 4 and form a precipitate of barium sulphate. The amount of turbidity formed is proportional to the sulphate concentration. When the timer expired, the UV-Vis was blanked with deionized water and pushed to zero then

followed reading of the prepared water samples. Phosphate test results was measured (read) at a wavelength 880nm.

Principle:

Orthophosphate and ammonium molybdate reacts with to produce a mixed complex molybdophosphoric acid. This complex is reduced by ascorbic acid giving an intense molybdenum blue colour.

3.5.4 Biological Parameter Testing

3.5.4.1 Total Coliform and E-Coli

(a) 3M Petrifilm Testing

This is water sample testing for total Coliform and E-coli, carried out using 3M petrifilm for both dry and wet season. The process involved pipetting 1ml of water sample into the 3M petrifilm ensuring no gas bubbles were formed as the film is covered and thereafter left in an incubator for 24hrs at 35°C. The incubation was done in duplicate and sheen colonies counted after 24hrs under magnification.

(b) Most probable number (MPN) Testing

Additionally, biological water quality analysis for the dry season only, incorporated the use of multiple fermentation tube techniques for faecal indicators and the results reported as a most probable number (MPN Index). MPN is an indication of the number of coliform bacteria that, more likely than any other number, would produce the test findings. It does not represent a count of the number of indicator bacteria present in the sample. It describes a collection of organisms that demonstrate faecal contamination; therefore, this study can only speculate that infections may be present. MPN of coliforms present in the water was determined by counting the number of positive tubes in relation to the MPN table based on conventional procedures for testing water and waste water (APHA, 2005).

Reagents

(a) Macconkey broth purple w/Bcp

Procedure

The MPN method of analysis uses tubes that contain a broth for bacterial growth. The test tubes were cleaned and an inner vial (Durham tubes) inverted and inserted inside the tubes. The Durham tubes will collect gas produced by the coliform bacteria.

Single strength broth was prepared by weighing 20 gram of Macconkey broth and mixed in a 500ml distilled water while the double strength broth was prepared by weighing 20 grams and dissolving in 250ml distilled water. 10ml of the single strength broth was added into 40 test tubes while 10ml of double strength broth was added into 20 test tubes with inverted vials. The tubes were thoroughly checked to ensure that the inner vial is full of liquid with no air bubbles. All the test tubes with broth were covered with foil papers and stem sterilized by autoclaving at 15lbs pressure (121°C) for 15mins. After sterilizing, under a sterilized laminar flow, the water samples were added into each tube and incubated the tubes for a 24hrs at 37°C. 0.1 ml and 1 ml of water samples were added to 20 separate tubes (containing single broth) respectively while 10ml of water sample was added to tubes containing the double broth. When the 24hrs incubation was completed, the number of positive tubes determines the most probable number of organisms in the sample. The result from the presumptive test is positive with yellow, cloudy tubes. The inner vials contained gas bubbles too, an indication of coliform bacteria present. The number of yellowish, cloudy tubes were counted, thereafter a confirmation test was carried to determine the presence of total coliforms or E.coli.

Confirmation Test

The confirmation medium was inoculated with bacteria cultivated from the presumptive test. The confirmation media is more selective for the organism of interest. For colonial morphology, nutrient agar was used while Eosin-Y methylene blue agar was used for coliform confirmation test. From each positive Macconkey broth tube, both agars were inoculated using a sterile wire loop to spread on the petri dish containing the agar and incubated for 24 hours.

3.5.4.2 BOD Determination of Samples

Water samples for BOD determination was carried out immediately after sample were collected and the analysis was determined by BOD₅ method using Hach Dilution method 8043 adapted from Standard Method for the Examination of Water and Wastewater. Special care was taken throughout reagent handling to avoid contamination.

Principle

The BOD test determines the quantity of dissolved oxygen required by living organisms for aerobic organic matter consumption. The test findings are used to assess the impact of waste discharges on the oxygen supplies of receiving waterways. A standard 5-day period is given for incubation of the sealed water sample. Then, the change in dissolved oxygen content is identified. The BOD value is calculated from the results of the dissolved oxygen tests.

Reagents

- (a) **Ferric Chloride Solution:** 0.125 g of Ferric Chloride was dissolved in water and topped to 1 litre.
- (b) **Calcium Chloride Solution:** 27.5 g of calcium chloride was dissolved in water and topped to 1 litre mark.
- (c) **Phosphate Buffer Solution:** 42.5 g potassium dihydrogen phosphate KH_2PO_4 was dissolved in 700 ml water and thereafter 8.8 g sodium hydroxide was added giving a solution of pH 7.2. 2 g of ammonium sulphate was added as well and diluted to 1 litre. The solution was kept in a refrigerator to decrease the rate of biological growth.
- (d) **Magnesium Sulphate:** 25mg was dissolved and topped up to 1 litre.

Dilution water:

1ml of each of the above listed solutions that follow was pipetted per litre of distilled water at 20°C into a bottle and shaken vigorously for 1minute to bubble air through it. This is to saturate with oxygen. A satisfactory distilled water when incubated with or without seed should not absorb more than 0.2 mg/liter of oxygen, that is to say that the DO of the dilution water must not change by more than 0.2 mg/L when incubated for 5days at 20°C.

Procedure

Water sample used in this study is river water and is assumed have enough bacteria and as such were not seeded. The DO of the undiluted sample were determined and five sample volumes (250ml) and pipetted into five 300ml Bod bottles, followed by filling each bottle completely with prepared dilution water. Care was taken to insert the stopper in each bottle to prevent trapped air bubbles. The bottle was inverted and the content mixed. The blank was prepared as well by filling another 300-ml BOD bottle to the brim with the prepared dilution water. DO probe was used to measure the oxygen concentration in each bottle as well as that of the blank and there after the stopper inserted carefully in each of the prepared sample bottles to prevent trapped air bubbles. A cap and a foil paper was added to cover the stopper to prevent evaporations. The prepared sample bottles were incubated at 20°C for 5 days. After 5 days, the remaining DO in each of the prepared samples were measured and BOD calculated.

3.5.4.3 Chemical Oxygen Demand (COD) Determination of Samples

Principle of the Method

The material was refluxed for two hours in conc. sulphuric acid with potassium dichromate and silver sulphate catalyst. The organic content in the sample decreased some of the dichromate, and the excess was detected by titration with ferrous ammonium sulphate and the 1,10-phenanthroline indicator

Reagents

- (a) **Standard potassium dichromate (N/8)=0.125N=0.0208M):** 6.129 g of potassium dichromate ($K_2Cr_2O_7$) primary standard grade, previously dried for 2 hours at 103°C was dissolved in distilled water and diluted to 1 litre. 1ml=mg oxygen
- (b) **Sulphuric acid / Saturated silver sulphate :** 5.5 g of Ag_2SO_4 in 50 % (500ml) conc. H_2SO_4 continuously stirred for 1hour to dissolve.
- (c) **Standard ferrous ammonium sulfate (0.125M):** 49 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ dissolved in distilled water in a 1000ml volumetric flask and 10ml conc. Sulphuric acid (H_2SO_4) was added, cooled and diluted to 1 Litre.
- (d) **Mercuric Sulphate ($Hg SO_4$):** Powdered Ag_2SO_4
- (e) **Conc. Sulphuric Acid (H_2SO_4)**

(f) **Ferrous 1, 10 Phenanthroline Indicator:** 3.47g Ferrous sulphate was dissolved in 500ml distilled water, 7.42g 1,10 Phenanthroline monohydrate added and the mixture shaken until dissolved.

(g) **Glass beads (boiling chips)**

Procedure

20 mL aliquot of well mixed water sample was pipetted into a 500 ml Erlenmeyer flask. 1 g of HgSO_4 was added and 5 mL of sulfuric acid and mixed thoroughly until all the mercuric sulfate dissolved. 10 mL of N/8 $\text{K}_2\text{Cr}_2\text{O}_7$ was added and 70 mL of sulfuric acid-silver sulfate solution carefully added while mixing gently. Glass beads was added to the reflux mixture to prevent bumping, which may be dangerous. Silver sulphate added served as a catalyst while mercuric sulphate addressed the interference of chlorine (Cl^-). The flask was attached to the condenser and the mixture refluxed for two hours. The condenser was disconnected and the contents transferred into a beaker, the organic matter present in the water sample was reduced by some portion of the dichromate used and the remaining excess portion was determined by titration with standard ferrous ammonium sulfate (FAS) using 3 drops of ferroin indicator. A blank test was also carried out using 20 ml of distilled water using the same reagents and procedures as above. Results were recorded and COD expressed as milligrams of oxygen absorbed from dichromate per litre of the water sample.

3.5 Quality Control Assurance

This study minimized bias and variability associated with environmental data by adhering to quality control plan laid. Part of this plan included execution of accuracy checks during sampling and post-sampling analysis, equipment checks, maintenance and calibration to ensure optimum efficiency. Triplicate samples were collected from the same site at almost the same time and analyzed at the same manner. This was to ensure basic quality data.

3.6 Statistical Data Analysis

The statistical package used to conduct this analysis was SPSS software (IBM version 23) to calculate average mean, standard deviation of the data from the water and sediment samples. Pearson's correlation (r) value was applied to show the degree of physicochemical, biological and metal association in river water.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Levels of Physiochemical Parameters of Water Samples in Dry and Wet Seasons

Average values of physiochemicals ; odour, pH, TDS, EC, turbidity and colour levels in the selected sites from Ndakaini Dam are shown in Table 4.1 while average levels for TSS, TS, total alkalinity, total hardness, calcium hardness and silicon are shown in Table 4.2 below.

4.1.1 Odour

Odor (obnoxious smell) is brought on by algae, bacteria, anthropogenic activities like wastewater effluents and chemical spills (Cho *et al.*, 2013), which ultimately contaminate both ground and surface waters. The odour (obnoxious smell) detected in these sites are according to this order GO>GI>CO>KI>KO while the centre of the dam is odour free (Table 4.1). The odour detected in sites GO and GI validates the elevated levels of total coliform counts detected in the sample, since high correlation between the two parameters has also been reported (Sugiura and Nakano,2000). In comparison of the two seasons, odour was detected more in dry season than in wet season.

Table 4.1: Physiochemical parameters of water samples in dry and wet seasons.

Sampling site	Odour	pH	TDS (mg/L)	Electrical conductivity ($\mu\text{s}/\text{cm}$)	Turbidity (NTU)	Colour (Pt-Co)
dry Season						
TI	Odourless	6.23 \pm 0.06	12.70 \pm 0.01	25.37 \pm 0.06	4.78 \pm 0.08	35.33 \pm 0.86
GI	Odour	6.07 \pm 0.07	9.03 \pm 0.06	18.01 \pm 0.01	4.13 \pm 0.01	33.00 \pm 0.00
KI	Odour	6.60 \pm 0.10	13.5 \pm 0.06	27.13 \pm 0.12	7.74 \pm 0.01	47.00 \pm 0.01
KO	Odour	6.37 \pm 0.06	8.6 \pm 0.02	17.26 \pm 0.02	0.85 \pm 0.01	8.00 \pm 0.00
GO	Odour	4.5 \pm 0.01	759.3 \pm 0.58	1514 \pm 0.00	1.96 \pm 0.00	16.00 \pm 0.00
CO	Odour	6.44 \pm 0.01	11.1 \pm 0.06	22.07 \pm 0.05	1.71 \pm 0.01	10.00 \pm 0.00
C	Odourless	6.27 \pm 0.06	8.9 \pm 0.06	17.59 \pm 0.06	0.59 \pm 0.01	BD
Eleft	Odourless	6.00 \pm 0.00	9.2 \pm 0.01	18.42 \pm 0.01	0.86 \pm 0.01	BD
Eright	Odourless	6.23 \pm 0.06	9.0 \pm 0.03	17.92 \pm 0.01	1.06 \pm 0.01	BD
Wet Season						
TI	Odourless	6.93 \pm 0.08	7.71 \pm 0.00	15.47 \pm 0.01	14.93 \pm 0.12	54.67 \pm 0.58
GI	Mild odour	6.78 \pm 0.18	7.94 \pm 0.01	15.85 \pm 0.01	9.95 \pm 0.01	77.17 \pm 0.76
KI	Mild odour	6.57 \pm 0.04	17.80 \pm 0.00	35.63 \pm 0.06	17.73 \pm 0.06	153.33 \pm 0.58
KO	Odourless	6.71 \pm 0.01	9.42 \pm 0.08	18.77 \pm 0.06	0.83 \pm 0.06	14.67 \pm 0.58
GO	Odour	5.79 \pm 0.18	103.03 \pm 0.06	204.67 \pm 0.58	8.41 \pm 0.00	69.33 \pm 0.58
CO	Odourless	6.66 \pm 0.03	9.78 \pm 0.01	19.57 \pm 0.01	20.02 \pm 0.00	164.67 \pm 0.58
C	Odorless	7.14 \pm 0.01	8.78 \pm 0.01	17.61 \pm 0.01	0.77 \pm 0.02	16.67 \pm 0.58
Eleft	Odourless	7.17 \pm 0.01	9.27 \pm 0.06	18.53 \pm 0.01	1.10 \pm 0.00	14.67 \pm 0.58
Eright	Odourless	7.08 \pm 0.07	8.93 \pm 0.06	17.33 \pm 0.06	0.94 \pm 0.01	14.67 \pm 0.58
Permissible value in drinking and surface water						
WHO Drinking water	Odour free	6.5-8.5	<1000	2500	5	15
KEBS (Portable treated)	Odour free	6.5-8.5	700	1500	5	15
KEBS (Portable natural)	Odour free	5.5-9.5	1500	2500	25	50

Source: WHO (2011), KEBS (KS EAS 12: 2014). BD = Below Detection

Table 4.2: Physiochemical parameters levels in water samples in dry and wet seasons

Sampling site	TSS (mg/L)	TS (mg/L)	Total Alkalinity (mg/L)	Total hardness (mg/L)	Calcium hardness (mg/L)	Silicon (mg/L)
Dry Season						
TI	10.7±0.58	23.40±0.00	29.7±0.6	24.7±0.6	5.00±0.10	10.00±0.02
GI	5.2±0.29	14.23±0.00	15.0± 1.0	10.0±1.0	4.97±0.06	8.00±0.03
KI	4.0±0.00	17.50±0.00	25.3±0.6	10.3±0.6	BD	16.02±0.05
KO	1.0±0.00	9.60±0.00	30.3±0.6	14.3±0.6	4.9±0.10	7.01±0.01
GO	4.0±0.00	763.3±0.01	BD	19.7±0.6	5.00±0.00	7.04±0.02
CO	6.8±0.29	17.90±0.00	35.0±1.0	14.7±0.6	4.97±0.06	9.02±0.01
C	BD	28.9±0.00	25.0±0.0	15.0±1.0	BD	7.01±0.01
Eleft	BD	9.20±0.00	24.7±0.6	10.0±1.0	BD	12.04±0.01
Eright	BD	9.00±0.05	20.0±0.0	10.3±0.6	BD	10.01±0.04
Wet Season						
TI	14.67±0.58	22.38±0.23	20.00±0.50	15.3±0.6	9.90± 0.10	13.00±0.01
GI	16.67±0.58	24.96±0.03	14.83±0.29	25.0±0.1	9.97±0.06	6.01±0.02
KI	33.00±0.05	50.00±0.46	20.00±0.00	15.0±0.1	5.00±0.00	19.00±0.03
KO	10.48±0.47	20.08±0.26	19.83±0.29	5.0±0.0	10.00±1.00	7.00±0.01
GO	14.33±0.58	117.33±0.58	BD	20.0±0.5	5.00±0.50	6.00±0.01
CO	47.01±0.01	56.55±0.54	34.67±0.58	5.0±0.0	9.90±0.10	13.00±0.04
C	1.00±0.00	9.79±0.01	20.33±0.58	19.7±0.6	10.00±1.00	6.30±0.02
Eleft	1.00±0.00	10.27±0.02	19.83±0.29	9.8±0.3	4.83±0.29	10.01±0.04
Eright	1.00±0.00	9.93±0.02	20.33±0.58	10.00±0.1	4.83±0.29	11.00±0.01
Permissible value in drinking and surface water						
WHO Drinking water	Not detectable	Not stated	500	300-600	200	50
KEBS (Portable treated)	Not detectable	Not stated	500	300	150	50
KEBS (Portable natural)	Not detectable	Not stated	500	600	150	

Source: WHO (2011), KEBS (KS EAS 12: 2014). BD = Below Detection

4.1.2 pH

The mean pH of water samples of the dry season ranged from 4.5 ± 0.01 - 6.60 ± 0.1 . Site GO inside the dam had the lowest pH values as compared to other sites along the tributaries in the dam catchment. For the wet season, mean pH of water samples analyzed in situ varied from 5.79 ± 0.18 - 7.17 ± 0.01 with Eleft site showing the highest level (Table 4.1). Interestingly to note is that site GO recorded lower PH value in both seasons. With exception to site GO, the pH values were within the permissible limits (5.5-9.5) set by Kenya Bureau of Standards (2014). For natural potable water and within the guideline limit 6.5-8.5 set by WHO (2011). Wet season had high pH level than the dry period (Figure 4.1). During the wet season, the pH inside the dam was neutral and slightly higher among other sites than in dry season. This is most likely due to the dilution effect that occurs in the river during the wet season and decrease in water volume due to evapotranspiration in dry season.

Higher and lower pH values have an impact to both biological and chemical process. pH level of water affects the solubility and toxicity of chemicals and heavy metals as most metals become more water soluble with lower pH. The seasonality pattern in the pH of Ndakaini Dam sampling stations is similar to that reported by Akpan (2004) for Qua Iboe River.

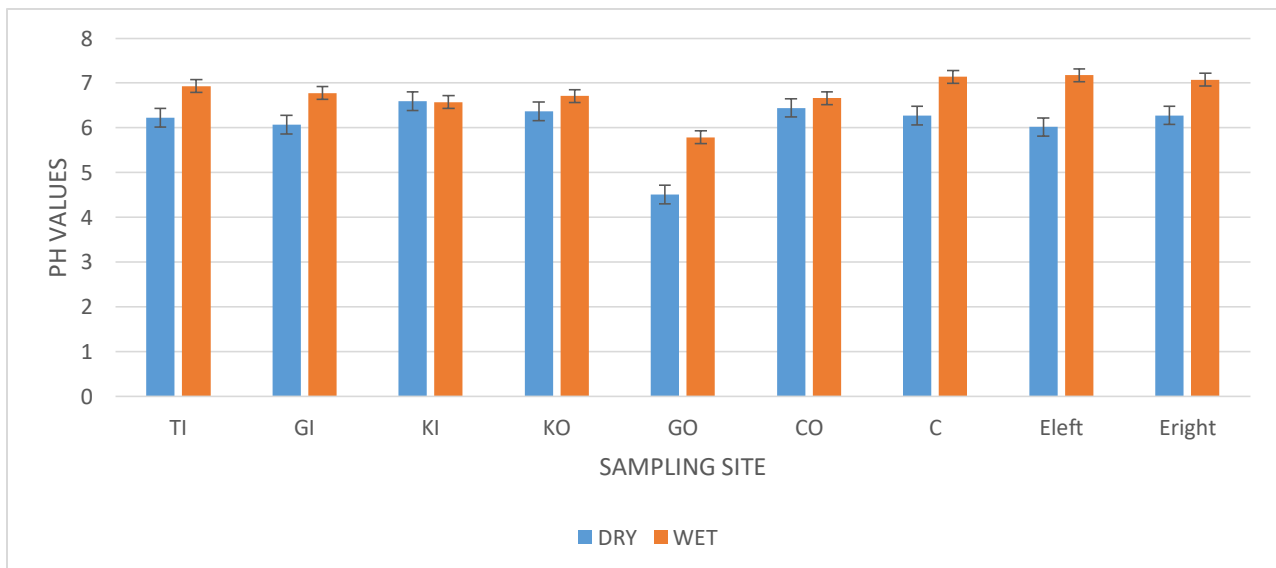


Figure 4.1: pH levels of water samples of selected sites in Ndakaini Dam.

4.1.3 Total Dissolved Solids (TDS)

The levels of TDS in water samples in this present study during the dry season ranged from 8.6 ± 0.02 - 759.3 ± 0.58 mg/L with GO site having the highest level and KO the least. The TDS levels of in water samples during wet season varied from 7.71 ± 0.00 - 103.03 ± 0.06 mg/L. TI showed lowest concentration of TDS while GO the highest (Figure 4.2).

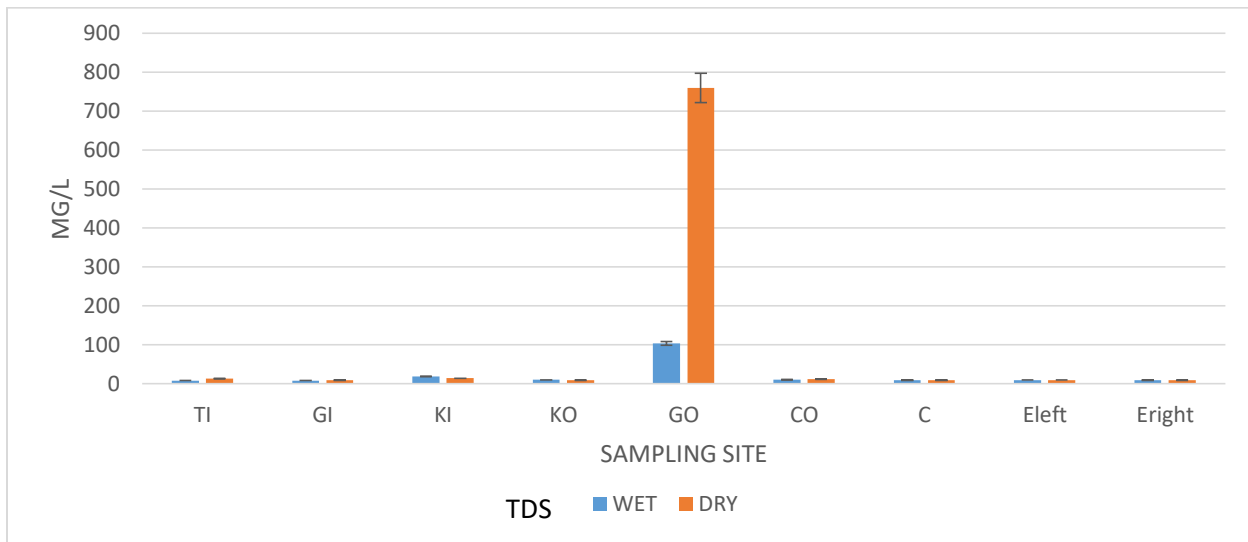


Figure 4.2: Total dissolved solids levels of water samples in selected sites in Ndakaini Dam.

In water, according to Mahananda (2010), total dissolved solids are mostly made of carbonates, bicarbonates, salts like chlorides, phosphates and nitrates of calcium, magnesium, sodium, potassium and manganese; as well as organic matter, salt and other different particles.

In both seasons, towards downstream; GO recorded the highest TDS level 759.3 mg/L (dry season) and 103.03 mg/L (wet season). This was followed by site KI 13.5 mg/L (dry season) and 17.80mg/l (wet season). This may be as a result of the heavy sediment deposit and anthropogenic activities going on downstream of these two sites. Additionally, the results of analysis at the sampling stations showed that dry season had higher mean values of total dissolved solids than in wet seasons (figure 4.2) and are well within the recommended limit of <1000 mg/L, by the WHO (2011) and 1500 mg/L for KEBS (2014) for natural potable water. Since the TDS and EC parameters are markers for salinity problems in water, (Schwab *et al.*, 1993), the low values of TDS in wet season and high TDS values dry season correlates well the levels of EC in all sampling stations. These results imply that river water from the sites in Ndakaini is good for domestic use as well as safe for drinking as it is free from laxative effects in humans; a condition caused by TDS

levels beyond 1000 mg/L (Sasikaran *et al*; (2012). Water for drinking purpose, the desirable TDS limit is 500 mg/L while maximum limit is 1000 mg/L. According to WHO, TDS values less than 300mg/L is excellent, between 300 and 600 is good but above 1000 mg/L is very poor and will produce undesirable taste in water (WHO, 2017).

4.1.4 Electrical Conductivity (EC)

Electrical conductivity levels for water samples varied between 17.26 ± 0.02 to 1514 ± 0.00 us/cm and 15.47 ± 0.01 to 204.67 ± 0.58 us/cm in the dry season and in wet season respectively, with site GO showing highest reading of electrical conductivity level for both dry seasons (1514 ± 0.00) us/cm and wet (204.67 ± 0.58) us/cm. as compared to the other sampling sites (Table 4.1).

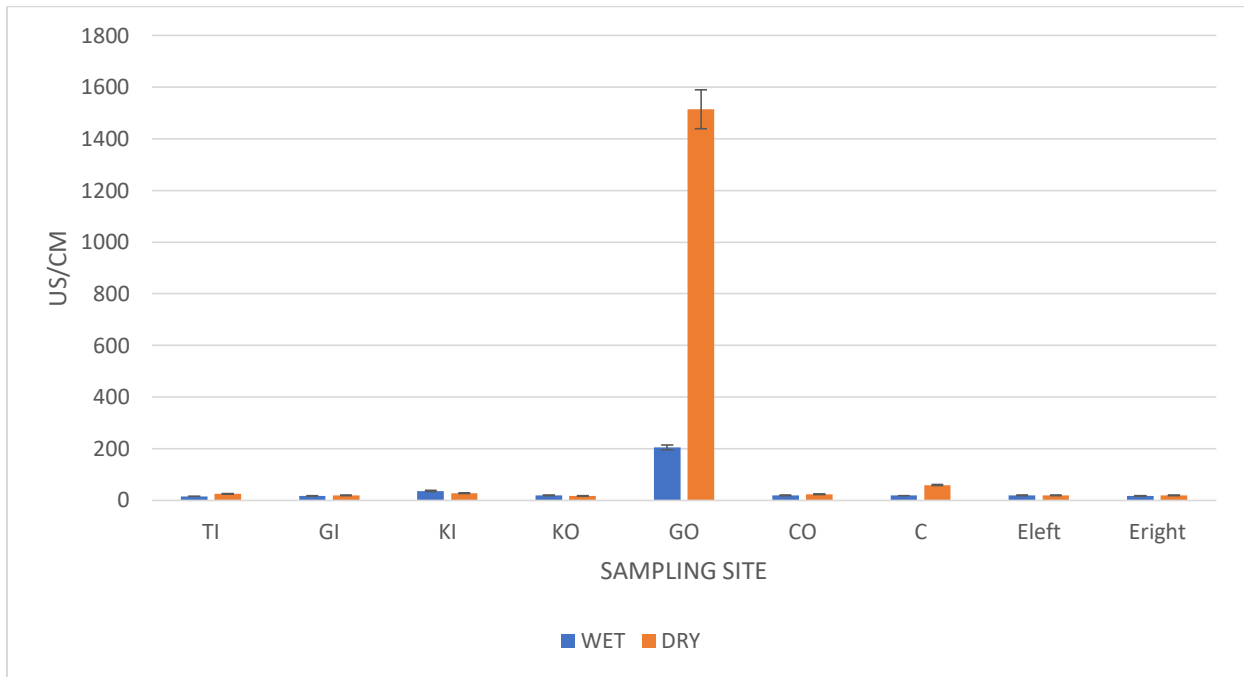


Figure 4.3: Electrical conductivity levels of water samples in sampling sites in Ndakaini Dam.

The result revealed higher levels of electrical conductivity recorded at site GO in both seasons (Figure. 4.3). The values across all sampling sites were much higher in the dry season than in the wet season except for inside dam where the values remained the same. The high level in dry season may be as a result of solution effects experienced in dry seasons. During the dry season, water evaporation causes a rise in concentration of ions in water, which in turn causes an increase in electrical conductivity. Similarly, in wet seasons, these concentrated ions dilute as a result of rain water. This is in agreement with Welcomme (1985) that regions with distinct dry and wet seasons,

the overall level of conductivity typically drops during the wet season because the water source is diluted. Although the total conductivity for the season is lower, conductivity surges are common when water first enters a floodplain. When a floodplain has soil that is mineralized or rich in nutrients, previously dry salt ions can become dissolved in solution during flooding thus increasing the conductivity of the water (Welcomme, 1985). For this study, there was no flooding during the period of sample collection. Also to note that since downpour (rain) water are mixed up with gases and dust particles, it may have a higher conductivity than pure water (Perlman, 2014).

Additionally, at any of the sites and in both seasons, the mean EC levels were within the permissible limit for river water quality for WHO (2018) direct abstraction (40–1500 $\mu\text{S}/\text{cm}$), WHO (2011) for portable water and KEBS (2014) limits for natural drinking water (2500 $\mu\text{S}/\text{cm}$) except during dry season for site GO (1514 \pm 0.00) where the EC was higher than the recommended WHO limits. According to Wetzel, (2001), Normal conductivity levels in water from the river and streams emanate from the surrounding geology. Clay soils do contribute to conductivity levels in water while granite bedrock does not. This may attribute to the higher levels of EC at site GO as this site is muddy. In addition, inputs from animal faecal discharge around GO site may contribute to its high EC values during both seasons.

4.1.5 Turbidity

Turbidity measurement of water reflects the transparency in water, an indicator of suspended substances or materials in water. In natural waters turbidity is mostly brought on by sediments, clay, phytoplankton organic materials and other microscopic organisms (EPA, 2012) that may be as a result of soil runoff. In this study, during the dry season, turbidity of water samples ranged from 0.59 \pm 0.01 to 7.74 \pm 0.01 NTU with KI site recording the highest concentration and C site the lowest concentration. Whereas in wet season, turbidity varied from 0.83 \pm 0.06 to 20.02 \pm 0.00 NTU with CO site showing the highest levels (Table 4.1).

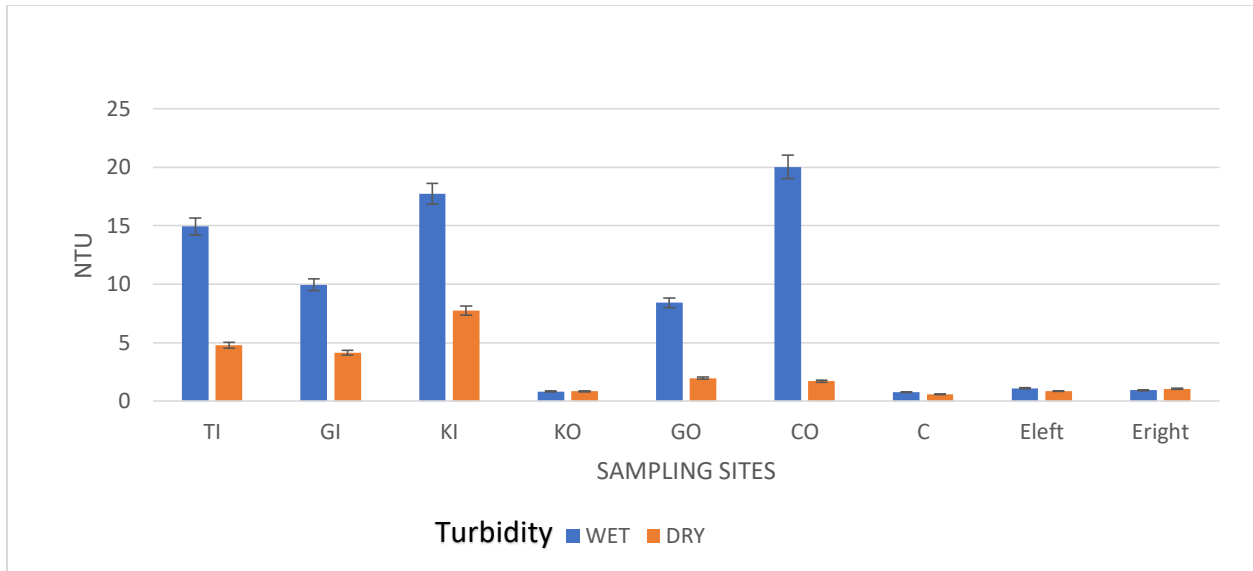


Figure 4.4: The Turbidity levels of water samples in selected sites in Ndakaini Dam

From figure 4.4 above, during the wet season, it's clear that turbidity was higher as compared to dry season. Site CO; which is an outlet from the dam showed highest turbidity during the wet season while KI site turbidity was high during the dry season. Four different sampling sites (KO, C, Eright and Eleft) showed low turbidity during wet and dry seasons. In Dry season, all the study sites recorded a low turbidity and are within WHO standard of 5 NTU except KI site (7.74 ± 0.01) exceeded the limit. The low mean turbidity of the river samples during dry season may be due to reduction in runoff material containing suspended and dissolved solids, precipitates and more so the recession in flow level in the dry season.

During wet season, four sites recorded very high turbidity levels above the WHO (2011) of 5NTU standard namely; GI (9.95 ± 0.01), TI (14.93 ± 0.12), KI (17.73 ± 0.06) and CO (20.02 ± 0.00) while the rest of the sites were approximately within 1 NTU. However, to guarantee effectiveness of disinfection, turbidity shouldn't exceed 1 NTU. Turbidity level at site CO in wet season may be due to high Sedimentation (due to high gravity flow rates) with presence of suspended particles. Additionally, due to the steep slope nature of the CO site and also bare soil where the riparian agricultural activities were taking place is likely to have increased the turbidity. Infiltration rate of water into the soil is slowed down by bare soils on steep slopes, and increase the rate of runoff at which top soils are washed into water bodies (Ran *et al*; 2012; He *et al*; 2015).

Findings of this study indicated that the mean values of turbidity did vary significantly between the two seasons; high in wet season and low in dry season and also showed high turbidity than the recommended WHO (2011) values in some sites as shown in Figure 4.5 However, in both seasons the turbidity values measured in all sites were within permissible KEBS limits (25 NTU) for Natural potable water. Following the WHO guideline, the usage of the water for drinking is quite unsafe but might be utilized for irrigation purposes depending on the type of irrigation technique to be employed.

High turbidity reduces the aesthetic quality of drinking water significantly. It can also increase the cost of drinking water treatment.

4.1.6 Colour

The result of this study for colour as shown on Table 4.1 ranges from BD - 47.00 ± 0.01 in dry season with site KI having the highest levels, followed by site TI (35.35 ± 0.86). While the sites within the dam (C, EL & ER) showed no colour detection (BD). In the wet season, Site CO had the highest level (164.67 ± 0.58) while KO, EL and ER had the lowest value (14.67 ± 0.58) (Table 4.1).

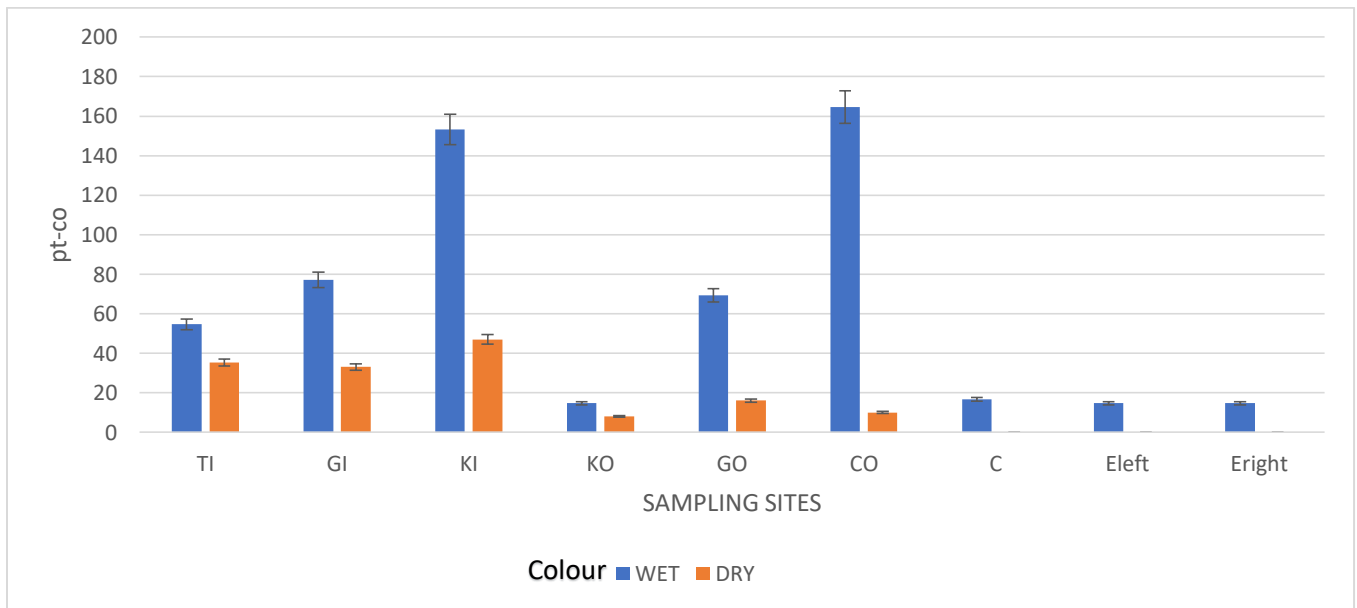


Figure 4.5: Colour levels of water samples in selected sites in Ndakaini Dam

It is evident from Figure 4.5 above, that higher mean colour levels were recorded in the wet season than in the dry season. This could be as a result of high runoff and prevalent agricultural activities with other anthropogenic activities in the wet season than dry season. Although there is no recommended health-based guideline value put forward for colour parameter in drinking water, levels below 15 NTU are often acceptable to consumers. Therefore, results indicates that in the tributaries downstream to the Ndakaini dam did not meet the WHO (2011) potable water standard of 15 NTU except for sites within the dam, CO and KO in dry season and sites KO, Eleft and Eright during the wet season. Site KO is a direct outlet from the dam hence explains the corresponding low colour as recorded inside the dam. However, the colour of water samples from the dam reservoir (sampling points C, Eright and Eleft) meets the minimum requirement of WHO standard in both season. This was possible due to settlement of flocculants and the retention time taken from the inlet tributaries feeding the dam reservoir during the dry season.

Additionally, the outcome of this study indicated that the colour values were all within the 50 NTU limit by KEBS (2014) for natural Portable water in the dry season. According to WHO (2011), colour in water is strongly by the presence of iron and other metals as natural impurities or from corrosive products, hence the colour levels correlates well with the levels of Iron in this study.

4.1.7 Total Suspended Solids (TSS)

TSS in water sample ranged from BD - 10.7 ± 0.6 mg/L in dry season with three sites (C, Eleft and Eright) showing absence of total suspended solids (BD). Site TI had the highest level (10.7 ± 0.6 mg/L) of TSS. In wet season, total suspended solids analyzed gravimetrically varied from 1.00 ± 0.0 to 47.00 ± 0.0 mg/L (Table 4.2).

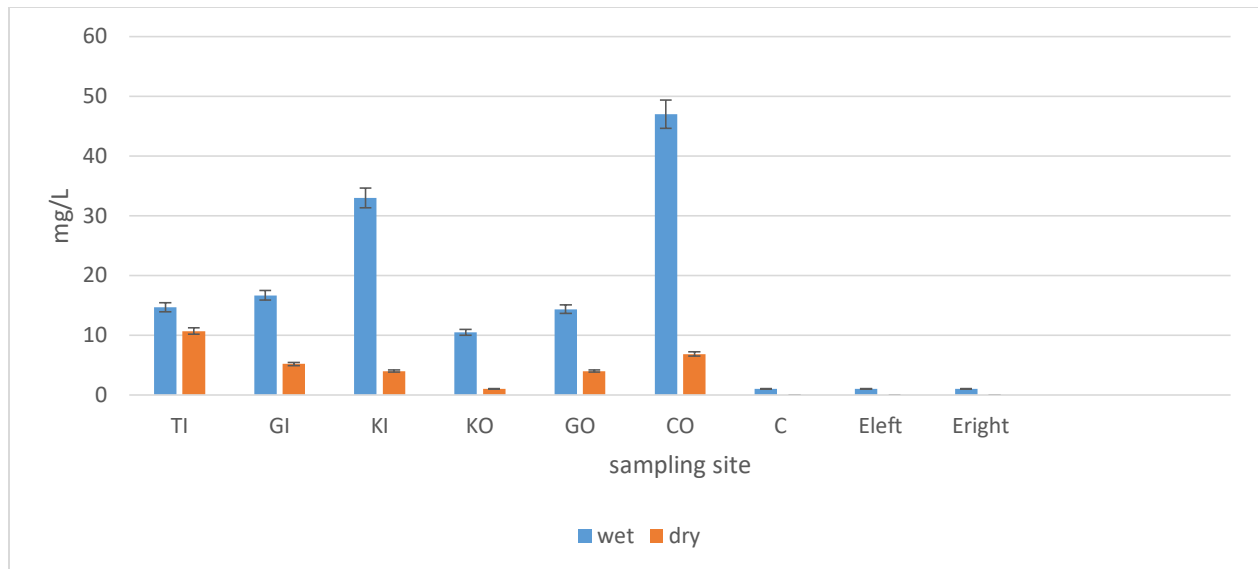


Figure 4.6: Total suspended solids levels in water samples in sites in Ndakaini Dam.

The seasonality profile of total suspended solids in Ndakaini Dam sampling sites indicated that levels were higher in wet season than in dry period (Figure 4.6). Higher values rainy season may be due to the influx of allochthonous materials into the rivers and dam reservoir through surface run-off (Akpan, 2004). Allochthonous materials are materials like rocks, minerals, limestones that are composed largely of organic debris formed elsewhere than in situ. In the wet season, TSS increased from 1.00 mg/L to 47.00 mg/L while in dry season it ranged from BDL - 10.02 mg/L. This is consistent with the work carried out by Akpan (2004) for Qua Iboe River. The decrease in the level of total suspended solids (TSS) in the dry season was probably due to decrease in sedimentation when the current velocity and water level was reduced as well. Comparatively, higher levels were considerably observed for most of the sites in the rainy season. However, the water courses from most sampling stations do not meet the WHO (2011) as well as KEBS (2014) drinking water standards of “undetectable” for natural potable, untreated water. Suspended particles, which are more naturally occurring than intentionally created, are primarily made up of algae, silt, and sediment. TSS is also affected by sediment resuspension caused by the characteristics of water flow and current type. However, excessive concentrations above the background value are the result of human involvement (Edori & Nna, 2018). Increased suspended particle levels in water indicate the extent of water contamination and are also responsible for several organoleptic qualities such as scent and colour (Edori and Kpee, 2016).

4.1.8 Total Solids (TS)

Total solids (TS) ranged from 9.60 ± 0.00 to 763.3 ± 0.01 mg/L in the dry season and in rainy season from 9.79 ± 0.01 to 117.33 ± 0.58 mg/L (Table 4.2). Total solids were higher during wet season across most sites (TI, GI, KI, KO and CO) as compared to dry season. On the other hand, the TS was particularly higher at site GO, in dry season as when compared to wet season (Figure 4.7).

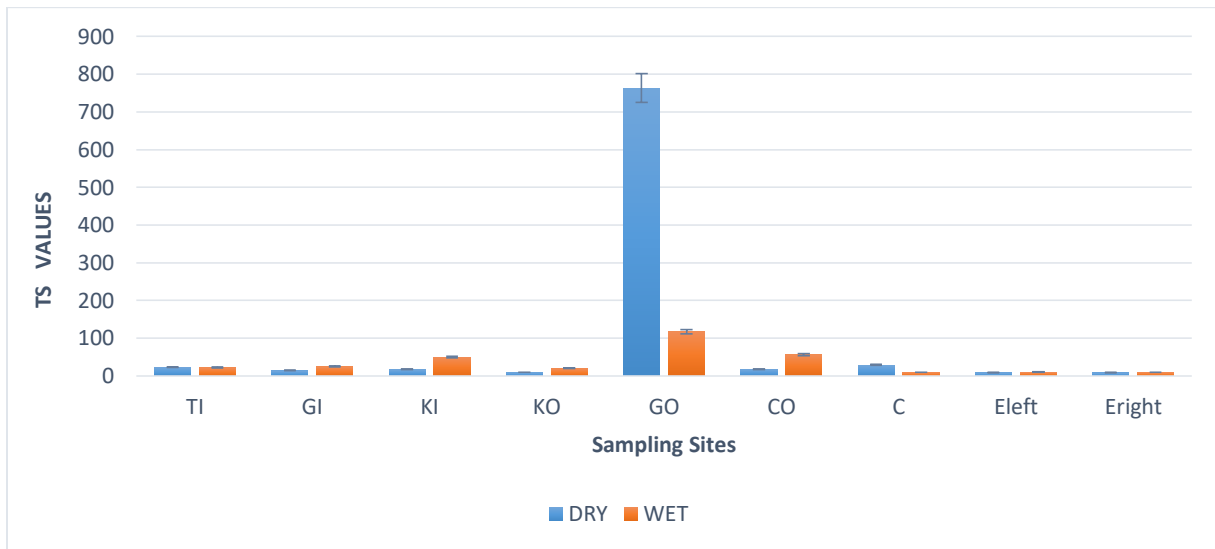


Figure 4.7: Total Solids levels in water sample in selected sites during wet and dry season

Total solid is a term used to refer to all the solids which are dissolved, hanged and settleable solids found inside of water. Total solids in high concentrations make drinking water unpalatable and can cause extreme health risks to human beings, terrestrial, aquatic plants and animals (WHO, 2006).

4.1.9 Total Alkalinity

The levels of total Alkalinity in dry season ranged from BD - 35.0 ± 1.0 mg/L. In wet season, it ranges from BD - 34.67 ± 0.6 mg/L (Table 4.2).

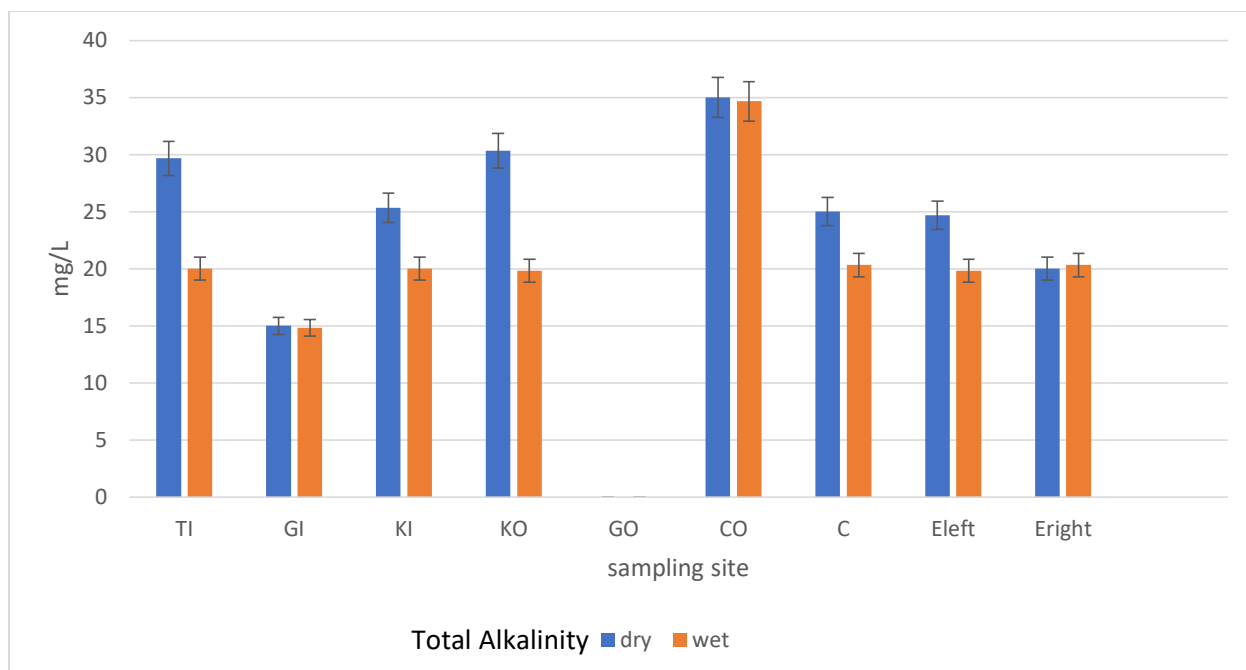


Figure 4.8: Total alkalinity levels of water samples in sites in wet and dry seasons.

In both seasons, total alkalinity was high in CO site while GO's site showed no levels at all. This may be influenced by the discharge of biodegradable waste that contained high nutrient (Chlorides, nitrates or sulphate), hence increasing the acidity level of GO site. Also, total alkalinity is higher in all sites and showed no significant variation.

Total alkalinity levels in all water sample tested were below KEBS (2014) and WHO (2008) acceptable limit for drinking waters (500 mg/L). These findings are consistent with the research conducted in Greece, where the alkalinity of the water varied from 23.56 to 267.00 mg/L (Spanos *et al.*, 2015).

4.1.10 Total Hardness

Total hardness level determined in the water samples during dry season ranged from 10.0 ± 1.0 to 24.7 ± 0.6 mg/L, site TI showed the highest value. In Wet season, total hardness of water samples from the nine sampling sites determined varied from 5.00 ± 0.0 to 25.0 ± 0.1 mg/L (Table 4.2).

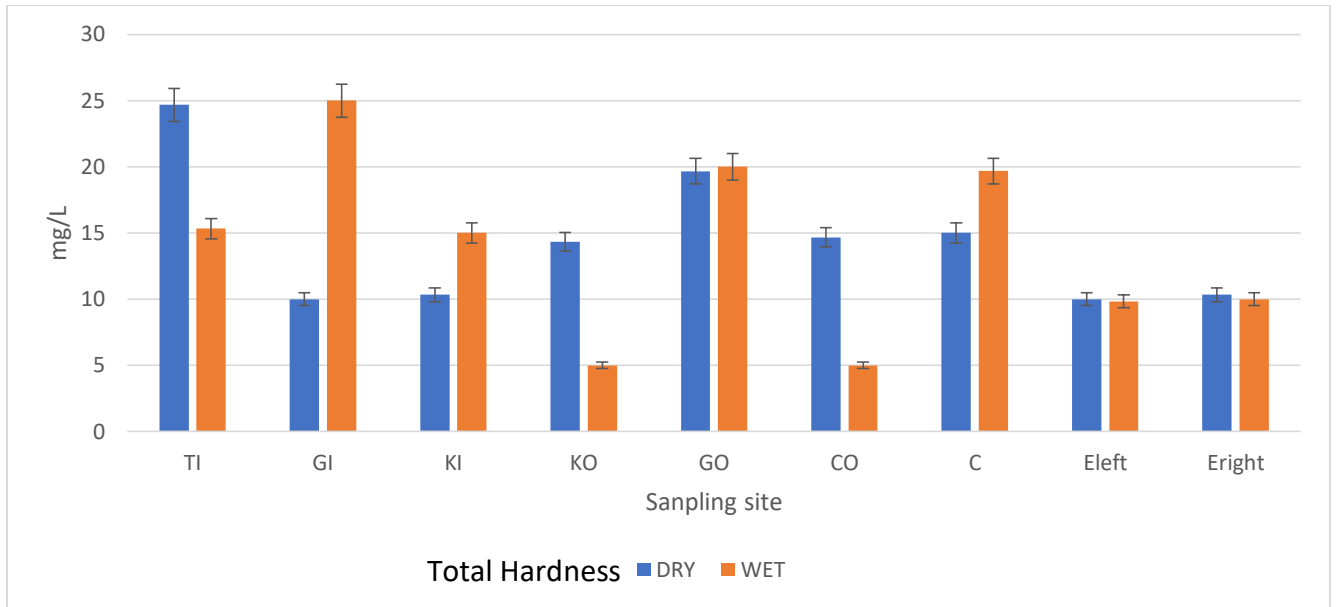


Figure 4.9: Total hardness levels of water samples in selected sites in Ndakaini Dam

In water, hardness is influenced by a range of dissolved metallic ions, primarily magnesium and calcium (EPA, 2001). From Figure 4.9, it's true to mention that all the nine sampling sites had total hardness in both wet and dry season. High total hardness level was recorded in GI site during wet season and TI site during dry season, however there was no trend in the readings of the total hardness for both seasons. Total hardness levels of water samples across all sites were below the WHO (2011) and KEBS (2014) recommended range of 300-600 mg/L for domestic water use. Subject to the interplay of other factors, such as pH as well as alkalinity, water with a hardness above 200 mg/L thereabout, may induce scale deposition in the treatment works, pipework, and distribution system and inside tanks within buildings. Also when heated, hard waters usually form deposits of calcium carbonate scale even in domestic boilers. Soft water (with hardness <100 mg/L) but not necessarily cation exchange softened water, may in contrast, have a low buffering capacity and hence be more corrosive for water pipes (WHO 2011).

4.1.11 Calcium Hardness

Calcium hardness is a metric that measures the amount of calcium ions present in the water. When water is referred as “hard”, it signifies the water is rich in mineral content. Chlorides or sulphates, calcium and magnesium carbonates, bicarbonates are what these minerals are largely made up of. These minerals mostly find their way into the water via washing over or through rocks of limestone and chalk (Gasmalla, 2015). The calcium hardness mean value was from BD – 5.00 ± 0.00 mg/L and from 5.00 ± 0.50 - 10.00 ± 1.00 mg/L in dry season and wet periods respectively. Kiama outlet had the highest mean levels (10.00 ± 1.00 mg/L) in wet season whereby four sites did not have any calcium levels (KI, C, Eright and E left) during dry season (Table 4.2).

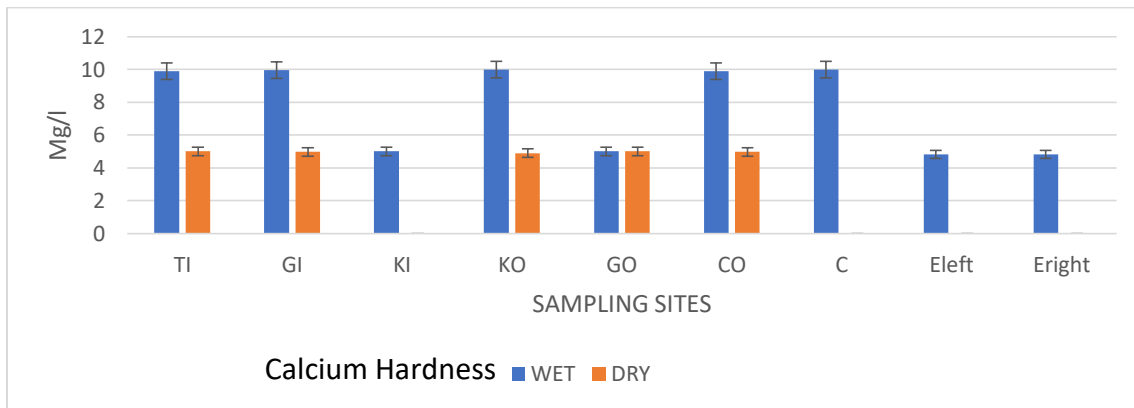


Figure 4.10: Calcium hardness levels in water samples in sites in Ndakaini Dam

The mean calcium hardness values increased slightly in the wet season, however, there was no amount analyzed in Sites KI, C, Eleft and Eright in dry seasons (Figure 4.10). The calcium hardness mean values at all sampling points are within 150 mg/L for both treated potable and natural potable permissible by KEBS (2014) and 200mg/L WHO (2011) limit. Based on the associated anion, taste threshold for calcium ion’s ranges from 100–300 mg/L (WHO, (2011).

4.1.12 Silicon (Si)

Silicon analysis was only carried out on water samples only. The mean levels of Si in water samples ranged from 7.01 ± 0.01 mg/L – 16.02 ± 0.05 mg/L during the dry season whereas in wet season, it varied from 6.00 ± 0.01 – 19.00 ± 0.03 mg/L. Similarly, a range of 0.5 – 19.3 mg/L result was obtained by Gbadebo *et al.*, (2013) in the ground water research.

From the result as presented in Figure 4.11 below, the Si level was higher in wet periods in majority of the sites as compared to dry season. Site KI had the highest Silicon levels in both seasons. The silicon levels in water samples across all sites during both seasons were below the WHO permissible limit of 50 mg/L.

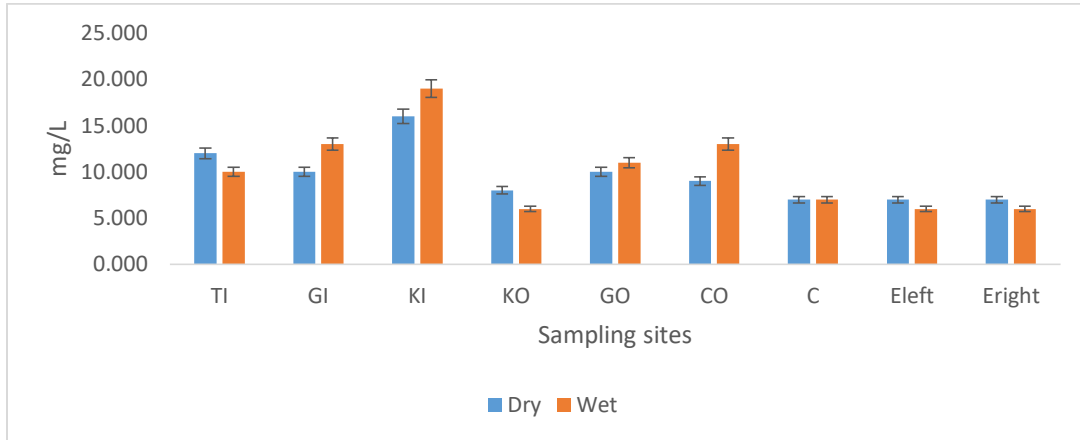


Figure 4.11: Si levels in water samples in sites in Ndakaini Dam

4.2 Levels of Biological Parameters of Water Samples in Dry and wet Seasons

The average values of the biological; Do, COD, BOD, E-coli, temperature and total coliform are shown in Table 4.3 below.

Table 4.3: Chemical and biological parameters levels in water sample during dry and wet seasons.

Sampling site	DO (mg/L)	COD (mg/L)	BOD (mg/L)	Temperature (°C)	Total Coliform (cfu/100 ml)	E-Coli (cfu/100 ml)
Dry Season						
TI	7.56 ±0.01	9.0 ±0.30	0.98±0.00	15.78±0.08	4.00±0.29	1.00 ±0.00
GI	7.49 ±0.01	5.2 ±0.00	1.91±0.00	18.17±0.06	2.0 ± 0.29	0.00 ±0.00
KI	7.38 ±0.03	5.78±0.00	1.00±0.01	18.27±0.06	7.0 ± 0.29	1.00 ±0.00
KO	5.86 ±0.01	1.3 ±0.04	0.40±0.01	18.90±0.00	10.0 ±0.00	0.00 ±0.00
GO	6.92 ±0.01	16.4±0.45	2.78±0.01	18.67±0.06	8.00±0.29	2.00 ±0.00
CO	7.39 ±0.01	6.3 ±0.00	1.3 ± 0.02	18.80±0.00	21.00±0.60	1.00 ±0.00
C	7.21 ±0.01	3.4 ±0.43	0.63±0.00	20.70±0.17	4.00 ±0.76	BD
Eleft	7.20 ±0.01	2.7 ± 0.15	0.74±0.02	20.07±0.06	4.00 ±0.00	1.00 ±0.00
Eright	7.10 ±0.06	3.3 ±0.15	0.59±0.01	19.50±0.00	5.0 ±0.60	1.00 ±0.00
Wet Season						
TI	7.83 ±0.05	5.60 ±1.09	1.72±0.006	15.50±0.50	12.00±0.00	0.00 ±0.00
GI	7.57 ±0.01	3.60 ±0.06	2.49 ±0.006	17.07±0.06	38.00±1.00	0.00 ±0.00
KI	7.26 ±0.03	5.80±0.01	1.25 ±0.006	17.47±0.06	22.33±0.60	1.00 ±0.00
KO	6.91 ±0.01	0.90±0.006	0.89 ±0.006	16.57±0.49	10.00±0.00	0.00 ±0.00
GO	7.68 ±0.01	6.60 ±1.09	4.65 ±0.006	16.17±0.29	47.00±0.00	4.00 ±0.00
CO	7.43 ±0.06	2.95 ±0.08	2.04 ±0.006	18.40±0.10	2.00 ±0.00	0.00 ±0.00
C	7.12 ±0.01	1.58 ±0.03	1.39 ±0.006	15.17±0.29	3.0 ± 0.60	BD
Eleft	7.00 ±0.10	1.90 ±0.00	1.57±0.010	16.80±0.10	5.0 ± 0.60	1.00 ±0.00
Eright	7.11 ±0.01	2.3 ±0.030	1.13 ±0.006	15.93±0.05	6.33 ±0.60	2.00 ±0.00
Permissible value in drinking and surface water						
WHO Drinking water	7	10	6	25-30°C	Not detectable	Not detectable
KEBS (Portable treated)	7	50	2	±3 °c of ambient temperature of the water body.	Not detectable	Not detectable
KEBS (Portable natural)	7	50	30	±3 °c of ambient temperature of the water body	Not detectable	Not detectable

Source: WHO (2011), KEBS (KS EAS 12: 2014). BD = Below Detection

4.2.1 Dissolved Oxygen (DO)

Table 4.3 shows the dissolved oxygen levels in water samples in dry periods which ranged from 5.86 ± 0.01 – 7.56 ± 0.01 mg/L. During the wet season, the levels ranged from 6.91 ± 0.01 – 7.83 ± 0.05 mg/L. In both seasons, the low DO levels recorded in Site KO may be as a result of poor aeration in the site. There was no remarkable seasonal difference in the mean dissolved oxygen levels in water samples across the sites observed (Figure 4.12).

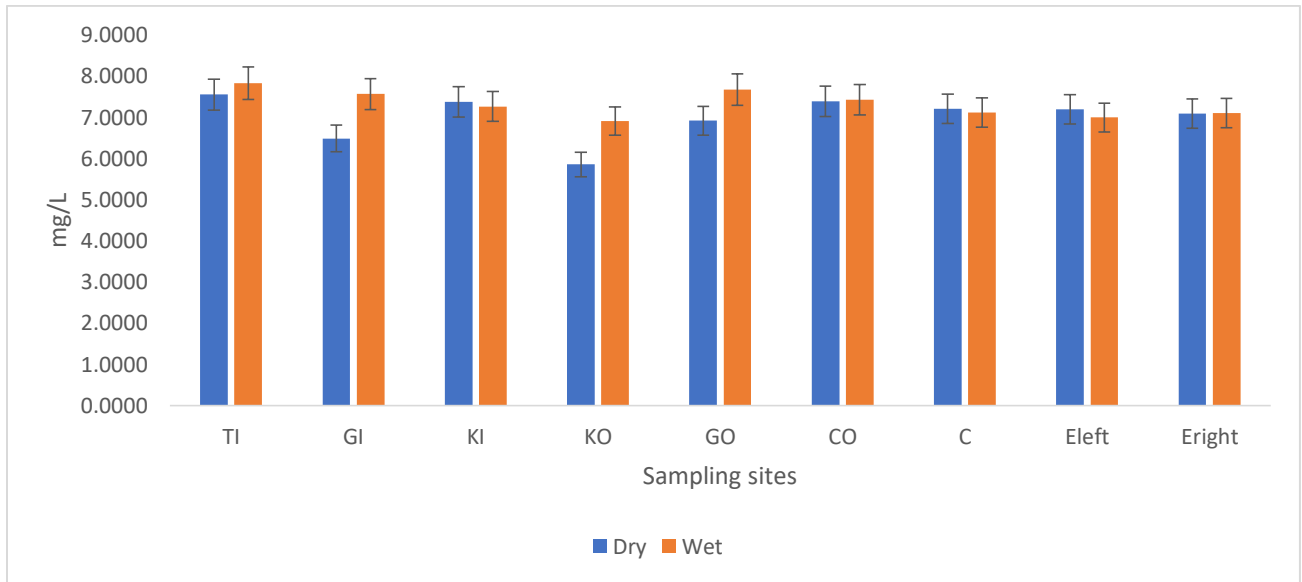


Figure 4.12: Dissolved oxygen levels in water samples in selected sites in Ndakaini Dam.

The dissolved oxygen levels among the sites (except within the dam) were slightly higher in wet than dry season. The DO values recorded from the sites studied in Ndakaini are within the expected range of natural fresh water (6-8 mg/L) and has the capability of support aquatic species like fishes. As stated in WHO (2011), there is no recommended health-based guideline for DO. According to WHO (2006), water set out for domestic purpose and recreational activities like bathing, swimming, boating and fishing should as well not be below 3.0 mg/L in DO concentration. The adequate levels of dissolved oxygen in the nine (9) sites of Ndakaini Dam location may be as a result of proper mixing of air through wind action as well as photosynthetic activity by aquatic plants and surrounding plants (Sila Onesmus, 2019).

4.2.2 Biological Oxygen Demand (BOD)

During dry season, biological oxygen demand (BOD) mean values varied from 0.40 ± 0.01 - 1.91 ± 0.00 mg/L, while the rainy season BOD levels ranged from 0.89 ± 0.006 to 4.65 ± 0.006 mg/L. (Table 4.3). Similar results (0.33 to 7.35 mg/L in wet season) were obtained by Ephraim and Ajayi (2015). The result in dry season showed that the BOD levels were lower as compared in wet season (Figure 4.13) and this may be as a result of the presence of increased amounts of pollutants such as pesticides, fertilizer and other nutrients from farmland (Kamarudin *et al.*, 2020) during run-off in wet season.

In BOD, the rates of oxygen consumption is directly proportional to the amount of degradable organic matter expressed as BOD therefore site GO with BOD of 4.65 ± 0.006 mg/L has a higher biodegradable organic matter as compared to site KO (0.89 ± 0.006 mg/L).

Spellman (2008) noted that the amount of dissolved oxygen in water bodies is directly impacted by biological oxygen demand. The higher the BOD, the faster the oxygen is depleted in the water, hence dissolved Oxygen decreases. From the study results, BOD mean values were below the permissible WHO (2008) range of 3-6 mg/L and KEB (2014) limit of 30 mg/L and 6 mg/L for natural and treated portable water respectively.

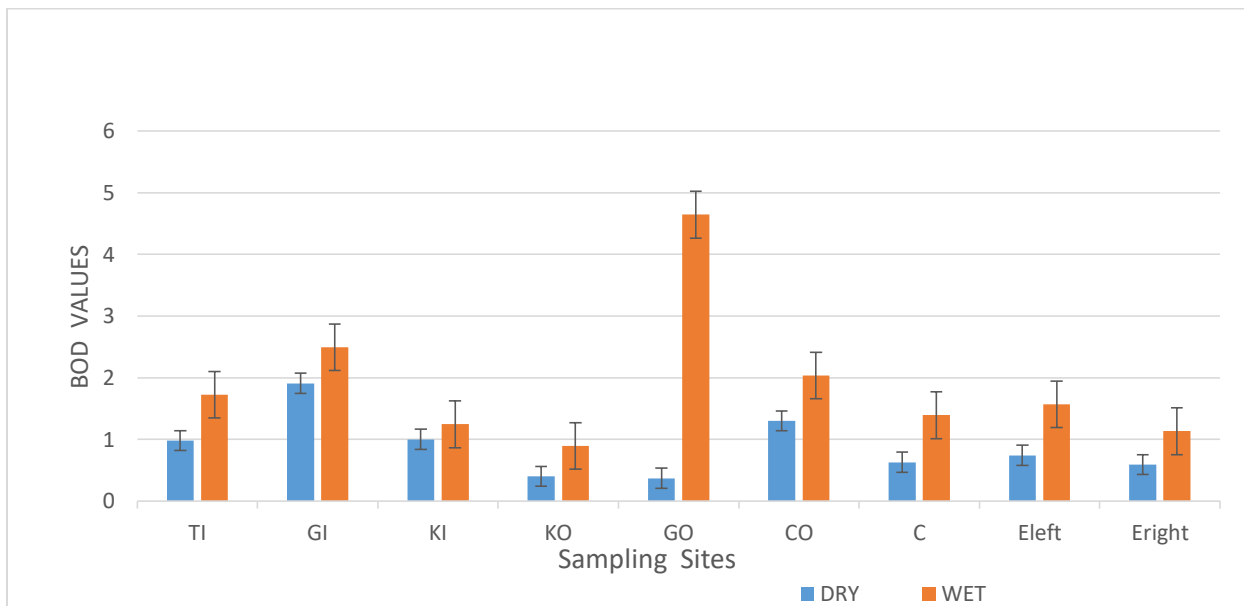


Figure 4.13: BOD levels of water samples in selected sites in Ndakaini Dam.

4.2.3 Chemical Oxygen Demand (COD)

The measure of Chemical Oxygen demand is a more effective test used to determining the organic pollution load in the water body and can be related to BOD (Wayne, 1997). From table 4.4 above, the mean (COD) during dry season was ranged from 1.3 ± 0.04 to 16.4 ± 0.45 mg/L and from 0.90 ± 0.006 to 6.60 ± 1.09 mg/L in wet season (Table 4.3).

In wet season, it was observed in site KO that the COD value (0.90 mg/l) is approximately equal to BOD value (0.89 mg/L). Owing to the fact that Site KO is a direct outlet from dam, this observation suggests that the organic matter in site KO is more of biodegradable matter.

Generally, these values are within the guideline value of 10 mg/L allowable by WHO (2010) and 50 mg/L by KEBS limits for natural potable water except site Go that recorded 16.4 mg/L in dry season. (Figure 4.13).

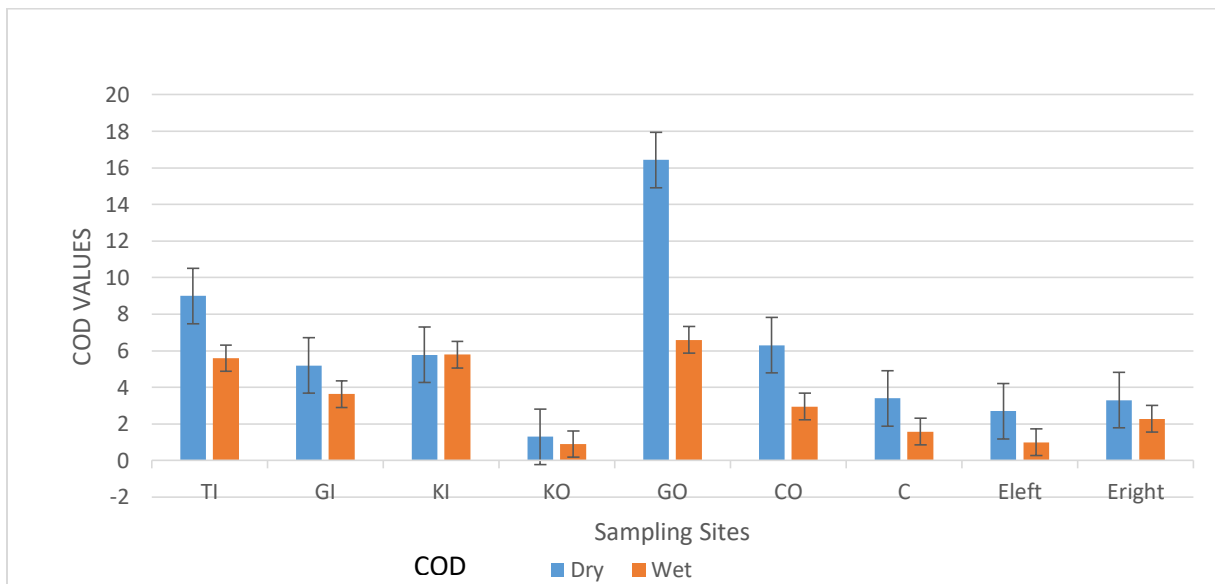


Figure 4.14: COD levels of water samples in selected sites in Ndakaini Dam

Temperature can be considered as one of the key determinants of water quality as it influences most chemical, physical and biological processes, such as chemical absorption, chlorine decay (Monteiro *et al.*, 2017) and changes in microbial growth. Temperature may increase problems associated to taste, colour, odour and corrosion. In Table 4.4, the mean temperature in dry season ranged between $15.78\pm 0.08^{\circ}\text{C}$ to $20.7\pm 0.17^{\circ}\text{C}$. Temperature recorded, was low in TI with

($15.78 \pm 0.08^\circ\text{C}$) and highest inside the dam (ER, C, EL). In wet season, the mean temperature varied from 15.50 ± 0.50 to $18.40 \pm 0.10^\circ\text{C}$ (Table 4.3).

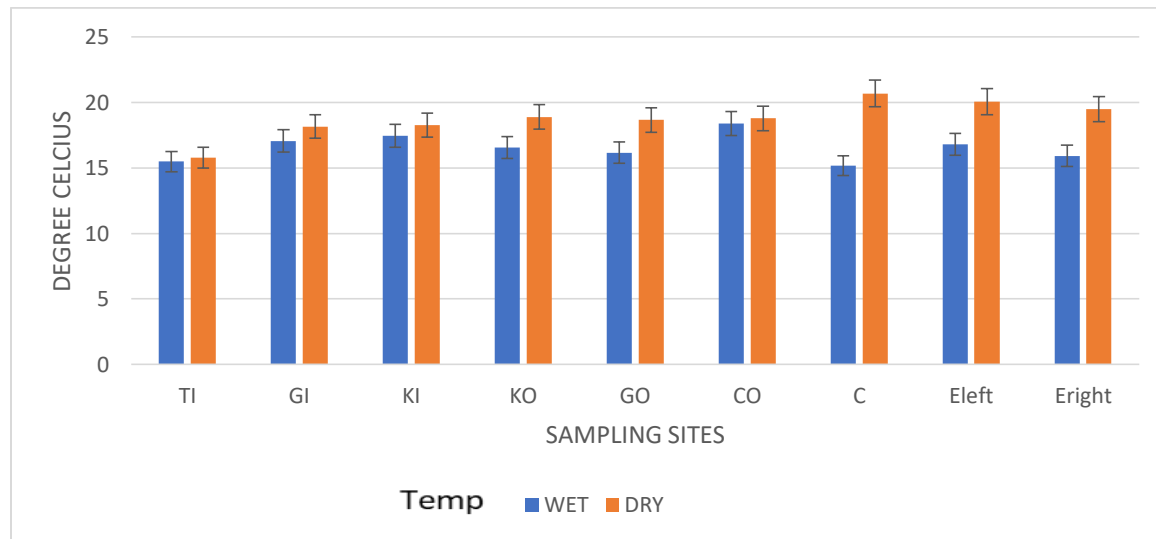


Figure 4.15: Temperature Levels of water samples in selected sites in Ndakaini Dam.

The temperature levels obtained in all the study sites are within the natural background range for water in the tropics which is $22\text{--}29^\circ\text{C}$ (Stumm and Morgan, 1981) and within the allowable limit of $25\text{--}30^\circ\text{C}$ for WHO drinking water guideline (WHO 2006) and KEBS (2014) limit. Ezeribe *et al.*, (2012) reported similar temperature level (29°C) of well water research in Nigeria. The lowest temperature was recorded at the TI sites followed by a gradual increase of temperature (Figure 4.15) downwards which was attributed to the fact that at higher altitude atmospheric air is cooler hence its immediate surrounding and another influence was change in the dam vegetation with a dense forest cover uplands giving way to less forest cover downwards. The temperature inside the dam was also significantly lower in the wet season than in the dry season because of increased precipitation. Variation in temperature in different sites can also be attributed to different timing of sample collection. Higher and lower temperatures can lead to undesirable biological effects.

4.2.5 Total Coliform and E. Coli (3M Petri film Results) for Dry and Wet season.

Coliform bacteria are organisms that occur in the environment as well as in the feces of all warm blooded animals and also humans, (Niyoyitungiye *et al.*, 2020). From figure 4.16a below, sheen colonies were formed after 24hrs of incubation and observed under magnification. The mean values for total coliform (TC) counts and E-coli in the various sites investigated in the wet season

were from $2.00 \pm 0.00 - 47.00 \pm 0.00$ and BDL – 4.00 ± 0.00 colony forming units (CFU) per 100 ml respectively while in the dry season, the levels total coliform and E-coli ranged from $2.0 \pm 0.29 - 21.00 \pm 0.60$ and BDL – 2.00 ± 0.00 CFU per 100 ml respectively (Table 4.3). The maximum mean E.coli detected was 4.00 ± 0.00 (CFU) at sampling point (GO) in the wet season. The coliform level observed in Ndakaini Dam was much lower than the reported coliform count in surface water by Onyango et al. (2018). The low counts of coliforms in the dam water were an indicator of the low pollution pointing to the presence of other pathogenic bacteria in low level (Onyango *et al.*, 2018).

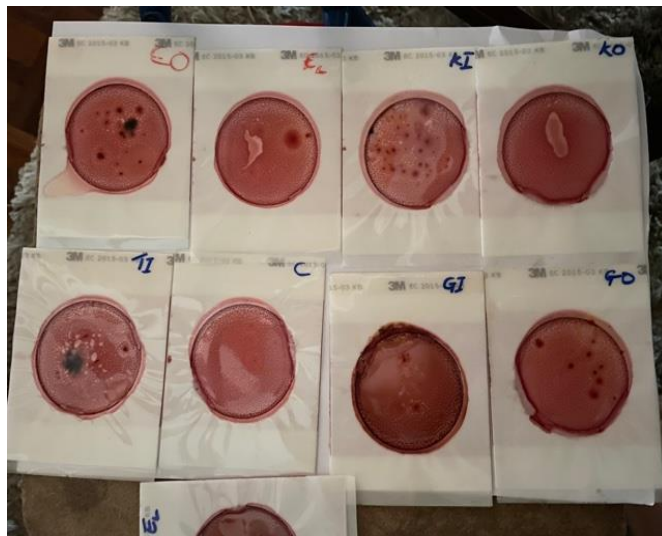


Figure 4.16a: 3M Petrifilm analysis of water samples of Ndakaini dam

4.2.6 Results of Most Probable Number (MPN) of Coliform for Wet Season

Biological water quality analysis for the dry season incorporated the use of multiple fermentation tube techniques for fecal indicators and the results reported as a most probable number (MPN Index). This is an index of the count of coliform bacteria that, more than any other number, would most likely produce the results shown by the test. However, it does not represent a count of the number of indicator bacteria that are actually present in the sample (Table 4.3). It reports a group of organisms that points the possibility of faecal contamination, therefore this study simply suggests that pathogens may be present. According to APHA (2005), the Most Probable Number (MPN) of coliforms present in the water during analysis was ascertained by the number tubes that turned positive (Figure 4.16b) in reference to the table of computation of MPN attached in

appendix 8. The indicator micro-organisms found in the sampling sites during the rainy season were as presented in table 4.4 below.



Figure 4.16b: MPN analysis of water samples of Ndakaini dam in wet season, before and after incubation

Table 4.4: Most Probable number (MPN) of coliform result during wet season

Sampling Sites	KI	CO	E _{Right}	GO	GI	KO	C	TI	E _{Left}
Mean Dry Season (MPN of Coliform per 100ml of the Original Water).	105	866	280	1,800	1,350	240	300	400	220

In the wet season, the most probable number of Coliforms was 1350, recorded at GO sampling site while the lowest was 105 recorded at the KI sampling site (Table 4.4).

The results show likelihood of pollution associated with fecal contamination brought on by human or o animals, suggesting that site GO is highly polluted from animal dung deposit inside the water, followed by site GI. According to Hosetti & Kumar (2002), the presence of coliform also suggests the potential that other pathogenic microorganisms may be present and further indicates the possibility of sewage contamination of river water source. This further agrees with WHO (2011)

that coliforms are found only in the mammalian intestinal tract. This contamination is likely to be as a result of raw sewage getting into the river system or most likely wastes from domestic animals.

Results obtained from this research have shown that most of the water sources in Ndakaini Dam sampling sites do not conform to the KEBS (2014) and WHO (2011) standards for potable water of “non-detected” for both E.coli and total coliform count. In essence, the river water sources from most of the sampling sites are not safe for household usage without prior disinfection.

4.3 Levels of Nutrient Parameters of Water Samples in Dry and Wet Seasons

The average values of the nutrients in water samples; sulphates, phosphates, chlorides, nitrates, fluorides and nitrites levels in the selected sites from Ndakaini Dam are shown in Table 4.5 below.

Table 4.5 Levels of Nutrient parameters of water samples in dry and wet seasons

Sampling site	sulphates (mg/L)	Phosphates (mg/L)	Chlorides (mg/L)	Nitrates (mg/L)	Fluorides (mg/L)	Nitrites (mg/L)
Dry Season						
TI	1.0±0.010	0.157±0.006	7.47±0.058	8.50±0.200	0.233±0.058	0.014±0.006
GI	1.0±0.001	0.227±0.006	7.47±0.058	5.20±0.100	0.233±0.058	0.022±0.007
KI	2.0±0.100	0.193±0.006	7.50 ±0.000	6.37±0.060	0.200±0.000	0.028±0.007
KO	BD	0.303±0.006	7.50 ±0.058	2.27±0.115	0.433±0.058	0.034±0.006
GO	1.33±0.570	0.200±0.387	7.47±0.058	106.7±0.058	0.233±0.058	0.668±0.010
CO	1.0±0.010	0.120±0.010	40.00 ±0.010	5.70±0.0580	0.200±0.010	0.05±0.001
C	BD	0.180±0.010	7.49±0.029	2.00±0.000	0.183±0.029	0.009±0.001
Eleft	BD	0.057±0.006	7.50±0.050	4.10±0.100	0.183±0.029	0.032±0.001
Eright	BD	0.143±0.006	7.52±0.029	4.50±0.058	0.193±0.012	0.031±0.002
Wet Season						
TI	3.97±0.058	BD	BD	17.33±0.058	2.00±0.50	0.030±0.001
GI	1.97±0.058	0.02±0.010	BD	7.833±0.058	1.00±0.01	0.037±0.003
KI	3.93±0.116	0.08±0.010	BD	17.13±0.058	1.00±0.00	0.085±0.005
KO	1.03±0.058	0.06±0.006	BD	2.67±0.058	0.567±0.01	0.013±0.003
GO	2.01±0.000	0.01±0.010	12.67±0.289	27.38±0.029	1.00±0.01	0.086±0.002
CO	6.77±0.025	0.263±0.035	BD	22.8±5.800	1.01±0.00	0.069±0.006
C	BD	0.163±0.006	BD	11.77±0.058	BD	0.016±0.002
Eleft	BD	0.183±0.006	BD	12.47±0.058	1.01±0.01	0.019±0.003
Eright	BD	0.15±0.006	BD	16±0.100	1.00±0.01	0.019±0.002
Permissible value in drinking and surface water(mg/L)						
WHO Drinking water	250	2	250	50	1.5	3
KEBS (Portable treated)	400	2.2	250	45	1.5	0.003
KEBS (Portable natural)	400	2.2	250	45	1.5	0.003

Source: WHO (2011), KEBS (KS EAS 12: 2014). BD = Below Detection

4.3.1 Sulphates

The sulphate level during the dry season ranged from BD – 2.0 ± 0.010 mg/L with the sites within the dam and site KO showing no record while in wet season, the values varied from BD – 6.77 ± 0.25 mg/L (Table 4.5). Sulphate levels of water samples during the wet season was higher than the dry season. (Figure 4.17).

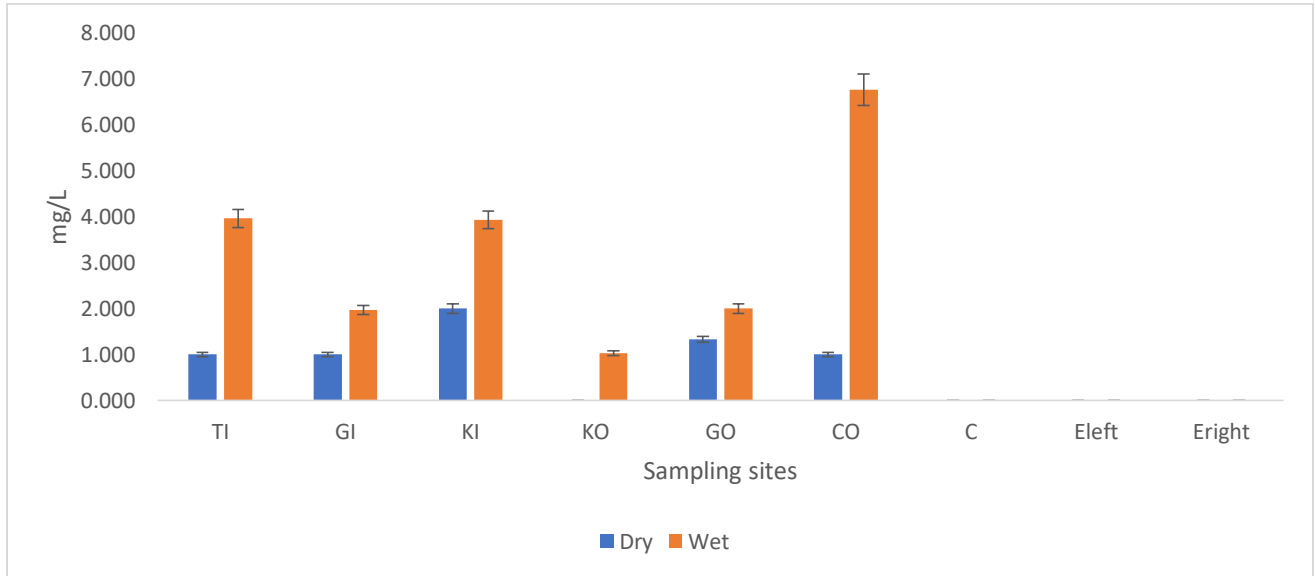


Figure 4.17: Sulphates levels in water samples in selected sites in dry and wet seasons

Sulphates are released into water through industrial wastes products as well as via deposits from the atmosphere. However, most elevated levels often occur in groundwater. Generally, the typical daily intake of sulphate from air, drinking water as well as food is in estimate of 500 mg per day, through meals as the major supply. This study indicates very low to non-detectable levels of sulphate ion in the nine (9) sampling sites with the maximum mean value observed at Chania outlet (6.77 ± 0.025 mg/L) during the wet season and 2.00 ± 0.100 mg/L at Kayuyu Inlet during dry season (Table 4.5). The concentration levels tend to increase slightly during the wet season. Also, no statistically, significant seasonal variation in mean sulfate levels in some of the sampling points. Nevertheless, the water samples were within the 250 mg/L permissible limits of WHO (2011) drinking water and 400 mg/L for KEBS (2014) for natural and treated portable water. While excess sulphate in water has no adverse effects or health implication (Popoola *et al.*, 2019), accumulation

of sulphate in water can cause an increased pH level, leading to Acidosis (Asamoah & Amarin, 2011).

4.3.2 Phosphates

From the analysis of nutrients in the water samples in dry season, phosphates levels varied from 0.057 ± 0.006 mg/L to 0.303 ± 0.006 mg/L and varied from BD - 0.263 ± 0.035 in wet season having levels high in CO site and low in TI (Table 4.5). Site TI had no phosphate levels during the wet season (Figure 4.18).

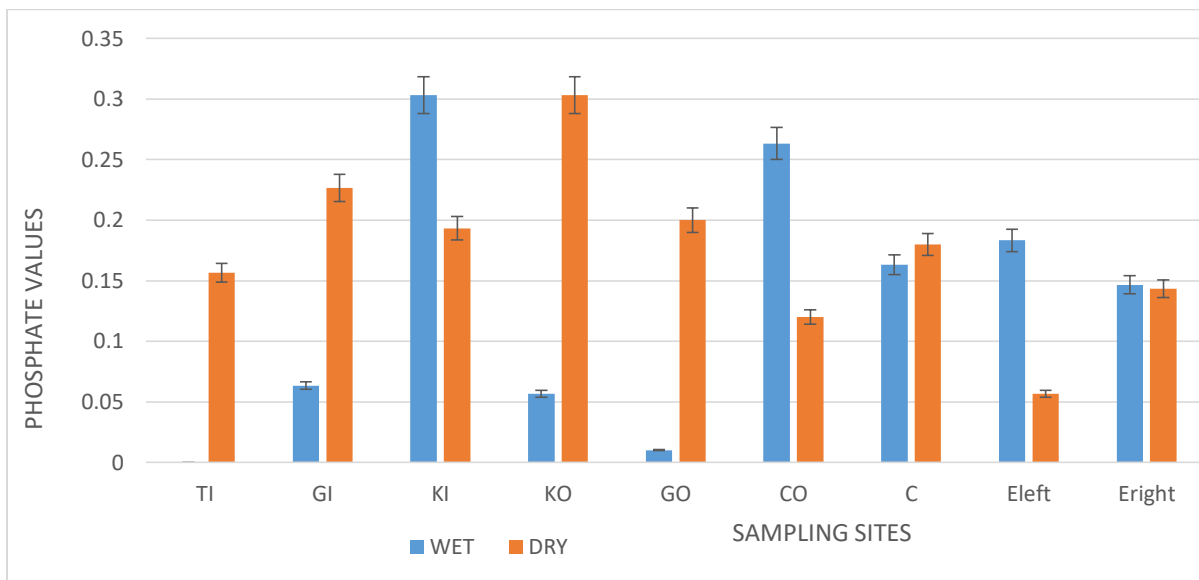


Figure 4.18: Phosphates levels in water samples in selected sites in dry and wet set seasons.

Phosphates is widely found in nature in plants, micro-organisms, domestic wastes and animal waste. Sources of phosphates in the environment comprise industrial discharges, domestic wastes, sewage, agricultural run-offs containing unutilized fertilizers and changes in land use in locations with naturally high phosphates content in the soil (Kenneth & Neeltje, 2002). Phosphates along with nitrogen (in the nitrate form) that enters into the water bodies do boosts the growth of algae as well as other plants resulting in blooms, slimes as well as significant variation in diurnal dissolved oxygen (EPA, 2001). The mean phosphate values from all sampling sites and in both seasons are within the 2.00 mg/L of WHO (2011) and 2.2mg/L KEBS (2014) permissible levels. The highest mean value was recorded at Chania Outlet (0.263 mg/L) in the wet season. This was most likely as a result of rain runoff containing fertilizer runoff during the wet season.

4.3.3 Chloride

In dry season, Chloride level varied from 7.47 ± 0.058 mg/L – 40 ± 0.010 mg/L. All the sites recorded approximately 7.5 mg/L except site CO which recorded the highest value of 40 ± 0.010 mg/L (Table 4.5). Whereas water samples had no chloride levels in wet season except site GO with a value of 12.67 ± 0.29 , however all the sites had chlorides in the dry season (Figure 4.19).

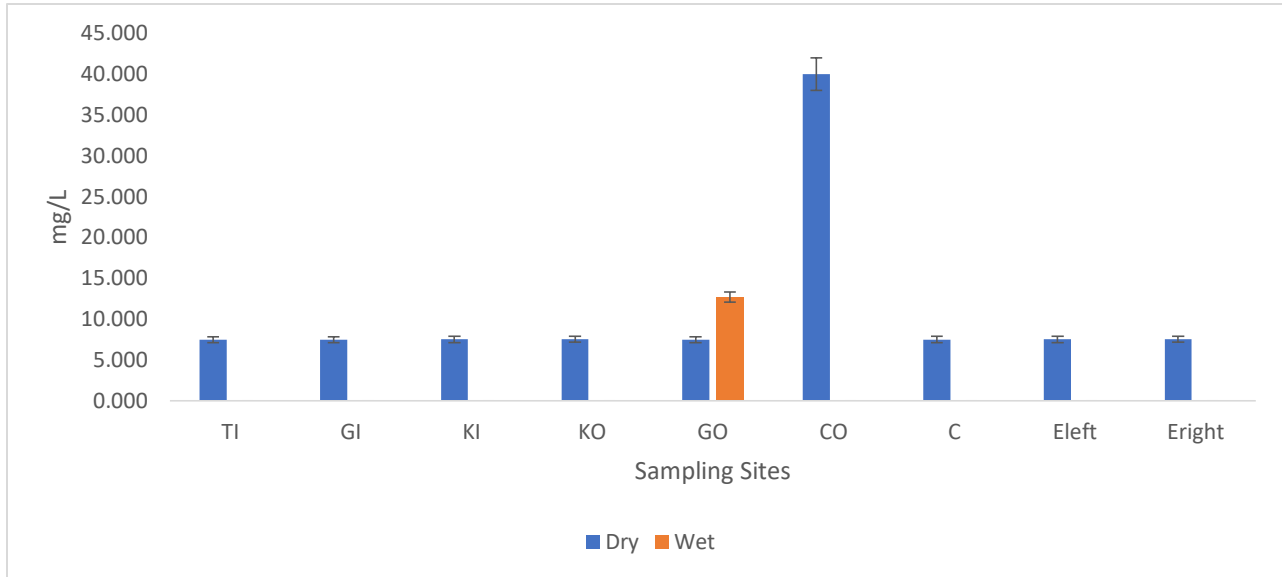


Figure 4.19: Chlorides levels in water samples in selected sites in wet and dry seasons.

Chloride (Cl^-) concentrations were elevated in the dry season than in wet season (figure 4.19). This may be as a result of high dilution of chloride due to high rainfall during rainy season. In both seasons, chloride levels in all the sampling sites from Ndakaini were below 250 mg/L guideline value permitted by KEBS (2014) and WHO (2011). Chloride (Cl^-) levels above 250 mg/L are most likely to be detected by taste (WHO, 2011). Depending on the water's alkalinity level, excess volume of chloride is known to increase the rate of corrosion for metals in the water distribution system (WHO, 2011).

4.3.4 Nitrates

As shown in Figure 4.20, the results showed minimum and maximum nitrate content levels of 2.00 and 106.7 mg/L for sites C and GO in the dry season respectively. In rainy season, the level of nitrate varied from 2.67 ± 0.058 to 27.38 ± 0.029 mg/L with site GO having the highest value in both season (Table 4.5).

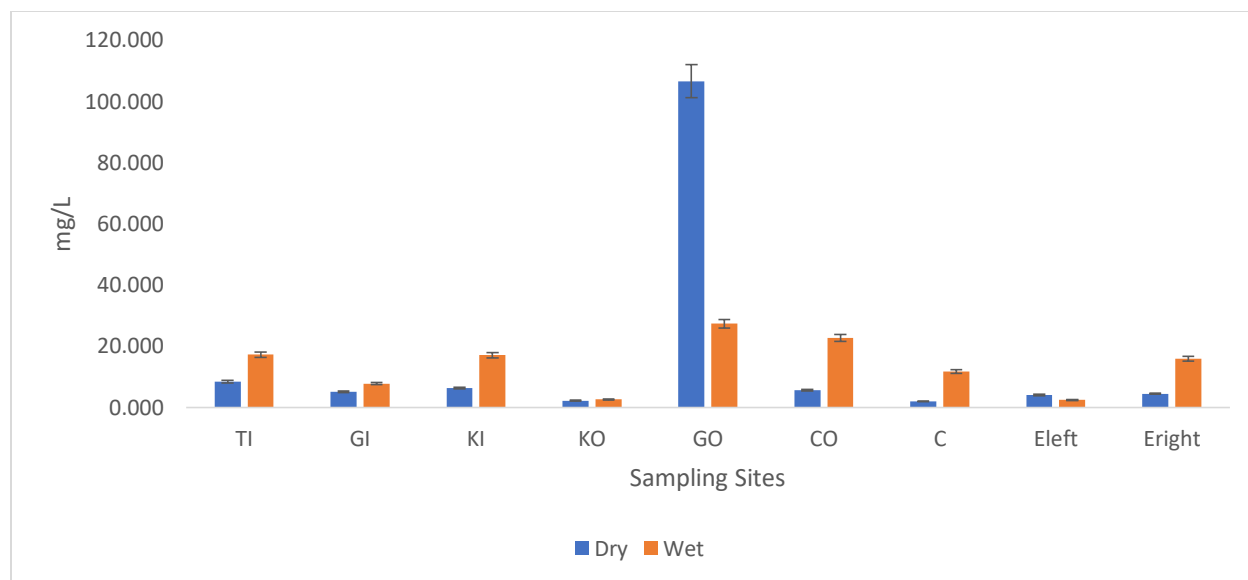


Figure 4.20: Nitrates levels in water samples in selected sites in wet and dry season

This high level of nitrification in site Gituru outlet (GO) during both seasons could be as a result of nomadic activity within the sampling location. Since there is no agricultural activities associated with fertilizer around Site GO, its high record of nitrate in dry season is likely to be due to animal waste discharge into the river, more so evapotranspiration effect in dry season and neutralization effect experienced in wet seasons. This is in agreement with Cave & Kolsky (1999) that high level of nitrate can be estimated to serve as a faecal pollution indicator where microbiological data are not available. This is because nitrate is being used by microorganisms as a food source. Generally, these results are comparable with earlier studies from Nigeria and Iraq by Mustapha (2008) and Al-Hasawi *et al.*, (2018) respectively. Nitrification processes in river water sources, can yield nitrate as well nitrites (Xia et al., 2004). Except for site GO value in the dry season, all other sampling sites had levels below the 50 mg/L (WHO, 2011) acceptable limit and 45 mg/L of KEBS (2014). Additionally, the nitrate values in rainy period were higher than in dry period probably due to agricultural practices around the sites and run-offs during wet season.

4.3.5 Fluorides

The results from the nine (9) sampling points portends low mean values of fluoride ion content in the water samples in both dry (0.183 – 0.433 mg/L) and wet season (0.567 – 2.00 mg/L) with the exception of the Thika Inlet (2.00 mg/L) in the wet season. This is due to agricultural activities

and runoff of fertilizer into the Thika River during the wet season. Additionally, mean fluoride ion values were slightly higher in the rainy season as compared to dry season (Figure 4.21).

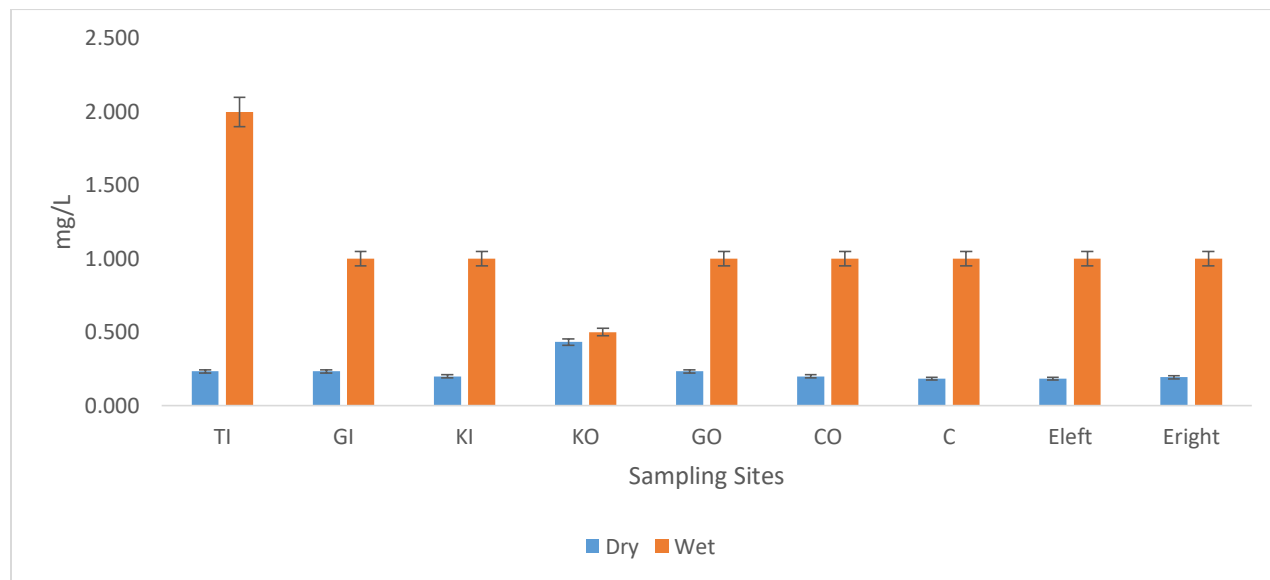


Figure 4.21: Fluorides levels in water samples in selected sites in wet and dry season

From the fluoride levels obtained in all the sampling sites, for both season, apart from Thika inlet in the wet season (2.0 mg/L) are within the permissible limits of WHO (2006) and KEBS (2014) of 1.5 mg/L standards for domestic water use.

This result is comparable to those gotten by Lalaury (2006) and Ravindra *et al.*, (2003), with record of having slightly higher fluoride concentration during wet periods than in the dry periods. Low flouride is essential to human as it helps calcification of dental enamel, however in excess of 1 mg/L concentration, it can lead to dental and skeletal fluorosis which can be severe (Laluraj & Gopinath, 2006).

4.3.6 Nitrites

From table 4.5 above, nitrite levels varied from 0.009 ± 0.001 mg/L - 0.668 ± 0.010 mg/L in dry period with highest value recorded in site GO while during wet period, the value varied from 0.013 ± 0.003 to 0.086 ± 0.002 mg/L with highest value from Site GO (Figure 4.22).

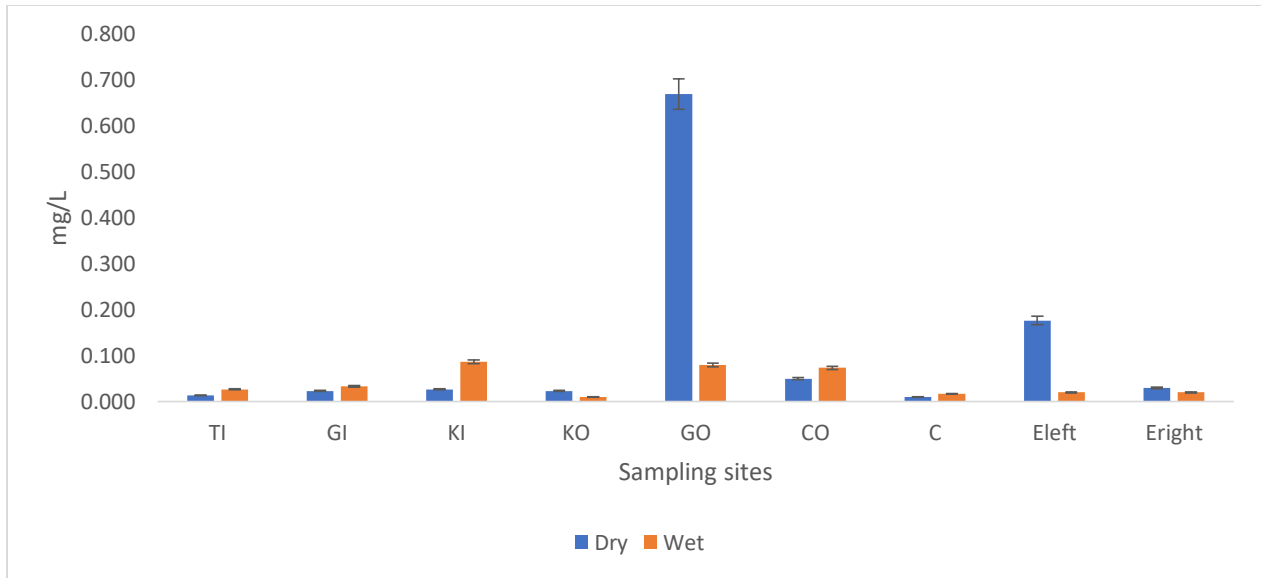


Figure 4.22: Nitrites levels in water samples in selected sites in wet and dry season

Also, all mean nitrite values were within 3mg/L permissible limit by WHO (2011), for drinking water but above KEBS (2014) limit of 0.003 mg/L for both treated and potable natural respectively; hence, making the water suitable for irrigation and domestic purposes.

4.4 Selected Heavy Metals Levels in Water and Sediments Samples During Dry and Wet Seasons

Sediments were accessible only in three (3) sites namely: KI, GI and GO, while other sites were deeply inaccessible. The average values of heavy metals in water and sediment samples; copper, lead, chromium, zinc, manganese, cadmium and iron levels in the selected sites from Ndakaini Dam are shown in Table 4.6 and 4.7 below. The results of the sediment quality analysis of heavy metal in this study samples were tabulated in Table 4.7 and were as well compared with three different international sediment quality guideline, namely: EPA heavy metal guideline for sediment (Ogbeibu et al., 2014), the screening levels guideline (SLG) of Ontario ministry of Environment (Canada) showing low and severe levels of toxicity and Interim Canadian Sediment Quality Guideline of the Canadian Council of Ministries of the Environment (CCME) showing the interim sediment quality goal.

Table 4.6: Selected heavy metal levels in water samples in dry and wet seasons.

Sampling sites	Cu (mgL ⁻¹)	Pb (mgL ⁻¹)	Cr (mgL ⁻¹)	Zn (mgL ⁻¹)	Mn (mgL ⁻¹)	Fe (mgL ⁻¹)	Cd (mgL ⁻¹)
Wet Season							
GI	0.042±0.002	0.3977±0.099	BD	0.1144±0.033	0.3632±0.005	2.6643±0.732	BD
KO	0.036±0.010	0.5266±0.015	BD	0.1324±0.026	0.5681±0.030	2.1227±0.958	BD
KI	0.049±0.009	0.4235±0.01	0.2885±0.01	0.1120±0.022	0.3254±0.020	0.5277±0.262	BD
C	0.036±0.004	0.3215±0.23	BD	0.1130±0.027	0.2831±0.020	0.3536±0.101	BD
Eright	0.045±0.011	0.1921±0.06	BD	0.087±0.028	0.2656±0.017	0.2516±0.039	BD
CO	0.031±0.016	0.3355±0.03	0.3141±0.04	0.0426±0.003	0.2629±0.026	0.3408±0.075	BD
Eleft	0.050±0.003	0.2318±0.064	BD	0.1109±0.054	0.2677±0.008	0.4289±0.126	BD
TI	0.367±0.275	0.4655±0.03	BD	0.1432±0.020	0.2959±0.027	0.552±0.224	BD
GO	0.046±0.015	0.3941±0.096	0.3722±0.137	0.1047±0.040	0.5105±0.032	2.343±0.108	BD
Dry Season							
GI	0.037±0.0017	0.0837±0.007	0.2233±0.035	0.0315±0.003	0.2172±0.024	0.9461±0.029	BD
KO	BD	0.0803±0.005	0.2100±0.007	0.1030±0.000	0.2167±0.021	0.7778±0.022	BD
KI	0.002±0.001	0.0785±0.0	0.2292±0.009	BD	0.2238±0.002	0.2669±0.002	BD
C	BD	0.0649±0.001	0.1694±0.015	0.088±0.004	0.1727±0.008	0.3202±0.019	BD
Eright	BD	0.1330±0.026	0.2116±0.018	0.085±0.000	0.2078±0.012	0.3611±0.010	BD
CO	0.046±0.00	0.0414±0.0	0.1735±0.009	0.115±0.029	0.1741±0.008	0.1823±0.003	BD
Eleft	BD	0.0427±0.003	0.1794±0.001	0.098±0.000	0.1789±0.008	0.2627±0.006	BD
TI	BD	0.0529±0.003	0.2087±0.006	0.065±0.000	0.2081±0.007	2.4011±0.027	BD
GO	0.035±0.011	0.0692±0.001	0.2051±0.006	0.0142±0.000	0.2057±0.005	1.0723±0.025	BD
Limits of Detection	0.002	0.005	0.01	0.01	0.0001	0.0018	0.001
Recommended values in drinking water							
WHO Drinking water	2.000	0.01	0.05	No guideline value	0.1 and 0.4 (health base)	0.3	0.003
WHO Surface water	1.000	0.01	0.05	5	0.1	0.3	0.005
KEBS (Portable treated)	1.000	0.01	0.05	5	0.1	0.3	0.005

Source: WHO (2011), KEBS (KS EAS 12: 2014). BD=Below Detection

Table 4.7: Selected heavy Metal levels in sediment samples in dry and wet seasons.

Sampling sites	Cu (mgkg ⁻¹)	Pb (mgkg ⁻¹)	Cr (mgkg ⁻¹)	Zn (mgkg ⁻¹)	Mn (mgkg ⁻¹)	Fe (mgkg ⁻¹)	Cd (mgkg ⁻¹)	
Dry season								
KI	11.87± 0.01	11.63± 0.10	58.48± 0.02	12.21±0.82	48.27±15.94	1627.98± 5.90	BD	
GI	20.55±0.002	31.33±0.03	78.87±0.05	21.99± 0.98	41.44±0.89	961.97± 13.4	BD	
GO	7.15± 0.02	10.46± 0.01	49.00±0.06	20.49± 0.37	47.53±14.45	1175.43±39.3	BD	
Wet Season								
KI	16.14± 0.09	55.03± 0.04	124.48±0.08	174.75±0.38	109.25±17.43	971.95±78.17	BD	
GI	21.93±0.09	97.84±0.31	133.57±0.04	295.38±1.14	78.90±7.68	1806.42±43.7	BD	
GO	19.25± 0.02	119.63±0.16	131.87±0.014	37.7±0.03	53.56±2.92	395.53± 8.9	BD	
Limits of Detection	0.002	0.001	0.005	0.01	0.0001	0.0018	BD	
Recommended guideline value in sediment								
Screening level guideline of Ontario Ministry of environment	Low	16.0	31.0	26.0	120.0	460.0	2.0	0.6
	Severe	110.0	250.0	110.0	820.0	1110.0	4.0	10
The (CCME) interim Sediment quality	ISQG	35.7	35.0	37.3	123	-	-	0.6
EPA heavy metal guideline for sediment (Ogbeibu et al., 2014)	Not polluted	<25	<40	<25	< 90	<300	NGV	-
	Moderately polluted	25-50	40-60	25-75	90-200	300-500	NGV	<6
	Heavily polluted	>50	>60	>75	>200	>500	NGV	>6

NGV =No Guideline Value. BD=Below Detection

4.4.1 Copper (Cu)

During the dry season, the results revealed that the levels of copper (Cu) in water samples ranged from BD - 0.046±0.00 mg/L while in wet season the levels ranged from 0.031±0.016 mg/L (Tables 4.6). There is no much difference in the levels of copper recorded in both season except that in dry season, most sites had levels of copper below the detection limit of 0.002 mg/L except site GI, KI, CO and GO (Figure 4.23a). The presence of copper in these sites may be as a result of the anthropogenic activity along the tributaries downstream. Also, the role of suspended sediment along these tributaries may have influenced the presence of copper levels in these sites. According

to Zheng *et al.*, (2008), seasonal variation of heavy metal loads in water are controlled by suspended sediment concentration as well as by the pH of water, which controls the absorbance of heavy metals. Some of the metals inside the dam water maybe trapped by sediment at the bottom, thereby decreasing the copper levels in the water sample.

However, the result shows that the level of copper in all water sampling sites were within permissible limits of 2 mg/L and 1 mg/L by WHO (2011) and KEBS (2014) standards respectively.

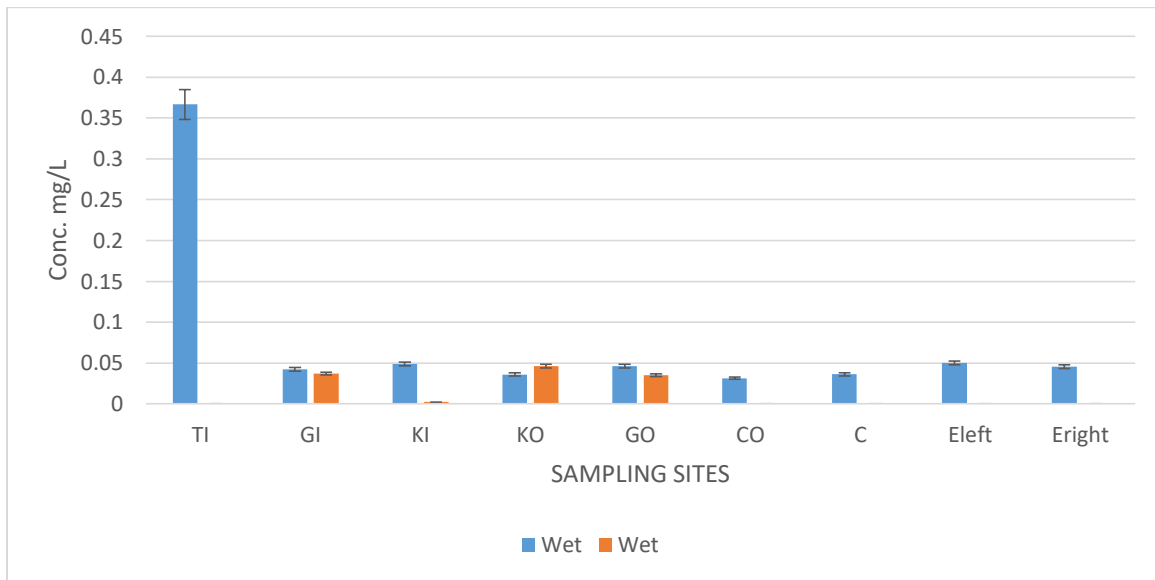


Figure 4.23a: Copper levels in water samples in selected sites in wet and dry season

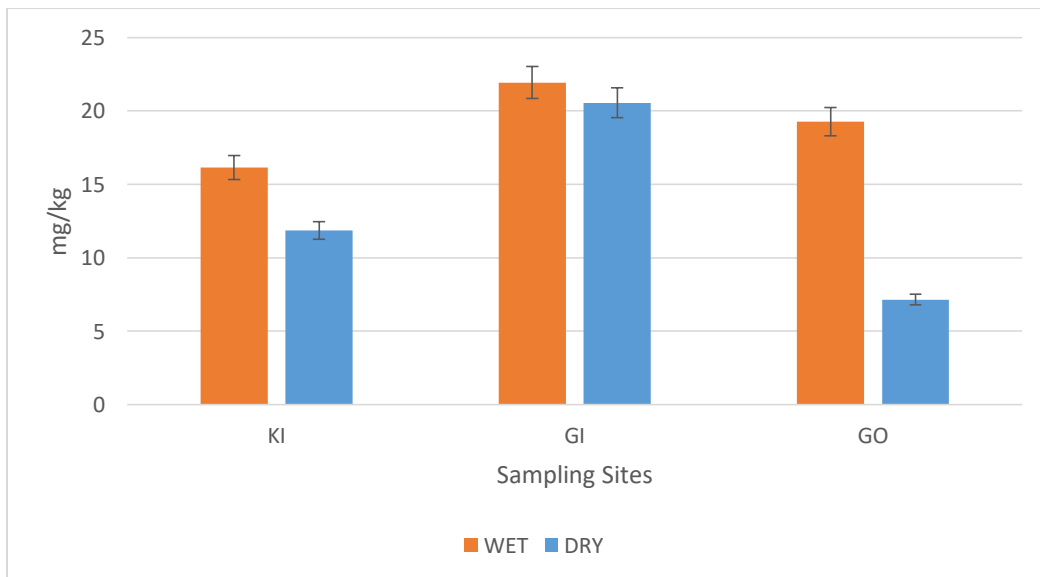


Figure 4.23b: Copper levels in sediment samples in selected sites in wet and dry season

In the sediment samples, the level of copper ranged from 7.15 ± 0.02 mg/kg – 21.93 ± 0.09 mg/kg (Table 4.7), showing higher levels in wet season (site GI 21.93 ± 0.09) than in dry season (Figure 23b). On comparison, it was found that copper sediment levels in both seasons were below the Environmental Protection Agency (EPA), Canadian Council of Ministers of the Environment (CCME) and Screening Levels Guidelines (SLG) of Ontario ministry of Environment, sediment quality guidelines.

Copper is hazardous even at very low quantities in water. When there is too much copper in the water (beyond the allowed limit), it causes gastrointestinal problems after a lengthy time of exposure in mammals, it is known to induce brain injury (Fatoki *et al.*, 2001).

4.4.2 Lead (Pb)

Level of lead in water samples from the Ndakaini Dam ranged from 0.0414 ± 0.00 – 0.133 ± 0.026 mg/L in dry season (Table 4.6) while during the wet season, water sample levels ranged from 0.1921 ± 0.06 mg/L – 0.5266 ± 0.015 mg/L. The levels of lead in water samples in all the sampling sites in the wet season showed a higher value of lead above the recommended guideline values of 0.01 mg/L by WHO (2011) and KEBS (2014) standards.

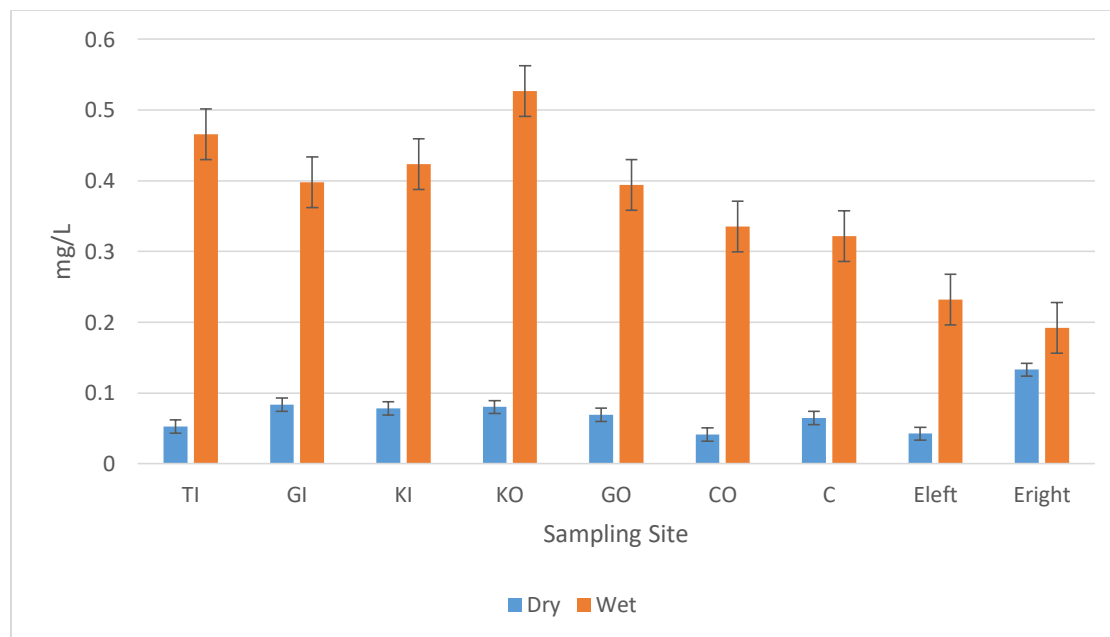


Figure 4.24a: Lead levels in water samples in selected sites in wet and dry season

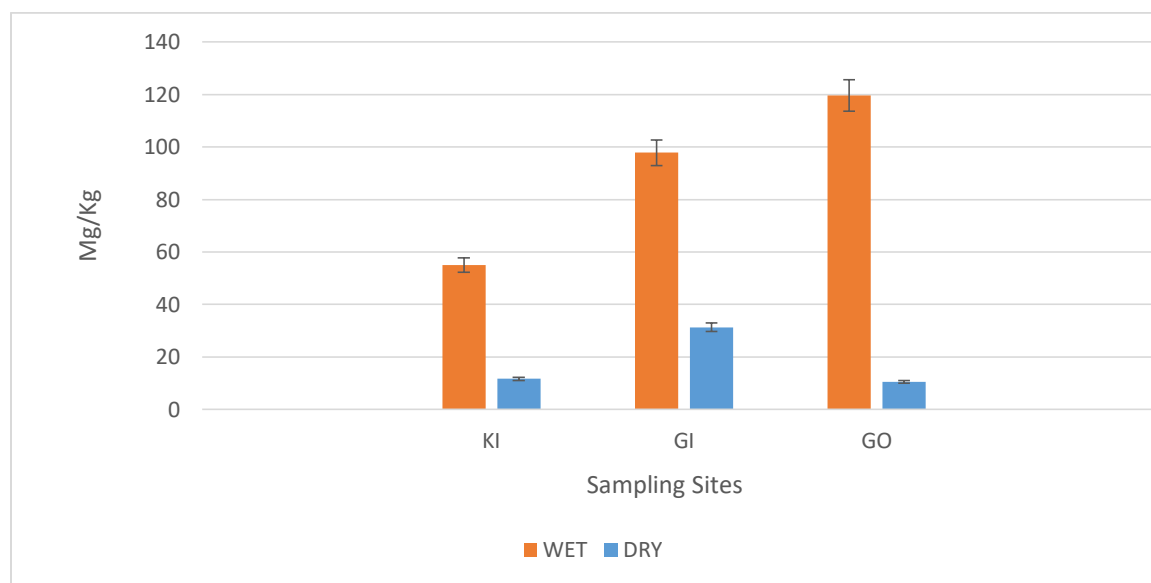


Figure 4.24b: Lead levels in sediments in selected sites in dry and wet seasons.

In sediment samples, the values varied from 10.46 ± 0.01 mg/kg – 119.63 ± 0.16 mg/kg (site GO) (Table 4.7). Lead levels in water samples were lower in dry season than in wet season and same trend was observed in the sediment samples (Figure 4.24a & 4.24b).

The level of lead in the sediment sample in all sites were below all the compared international sediment quality guideline authorities except the levels in wet season that were heavily polluted according to EPA sediment quality guideline (Ogbeibu *et al.*, 2014).

The presence of Pb in the sediments could be attributed to flocculation of lead-laden effluents released into watercourses, which were then washed down into the dam. The United States Environmental Protection Agency (USEPA) has categorized lead (Pb) to be potentially very harmful to most forms of life (USEPA, 1986). Hypertension, interference with calcium and vitamin D metabolism, developmental delay in the brain of fetuses and young children, tissue and damage in human's organs, and other numerous problems could result from the presence of lead in water over the allowed amount (Popoola *et al.*, 2019). More so, lead has been found to be carcinogenic (Hashim *et al.*, 2011).

4.4.3 Chromium

In dry season, all the sampling sites had levels of Cr higher than all guideline values. In the season, values in all sites conformed except at sites KI, CO and GO whose values were above the guideline

values. (Table 4.6 & Figure 4.25a). From the results, the detected levels of chromium in all sites were higher than the KEBS (2014) and 0.05 mg/L allowed limit by (WHO, 2011).

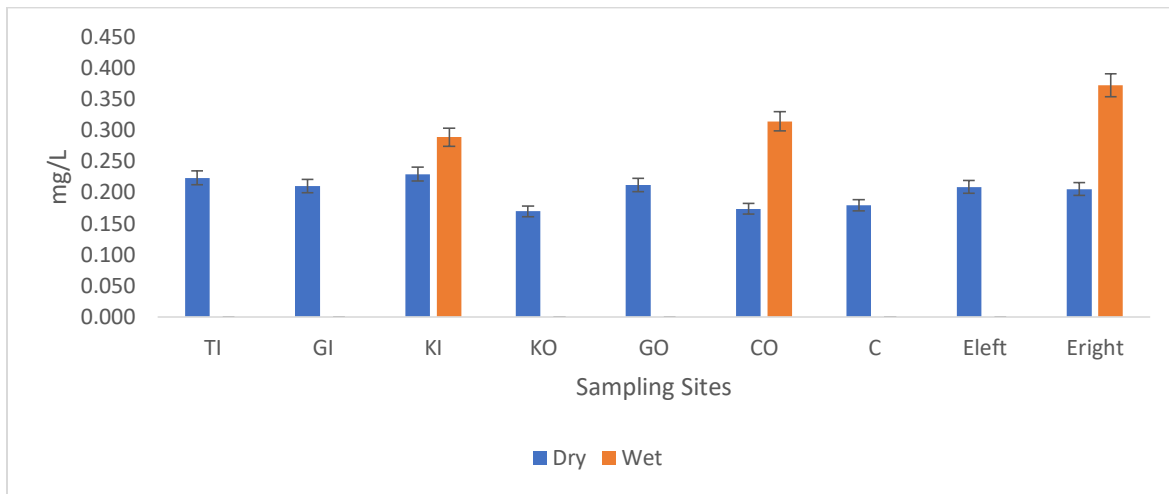


Figure 4.25a: Chromium levels in water samples in selected sites in dry and wet seasons

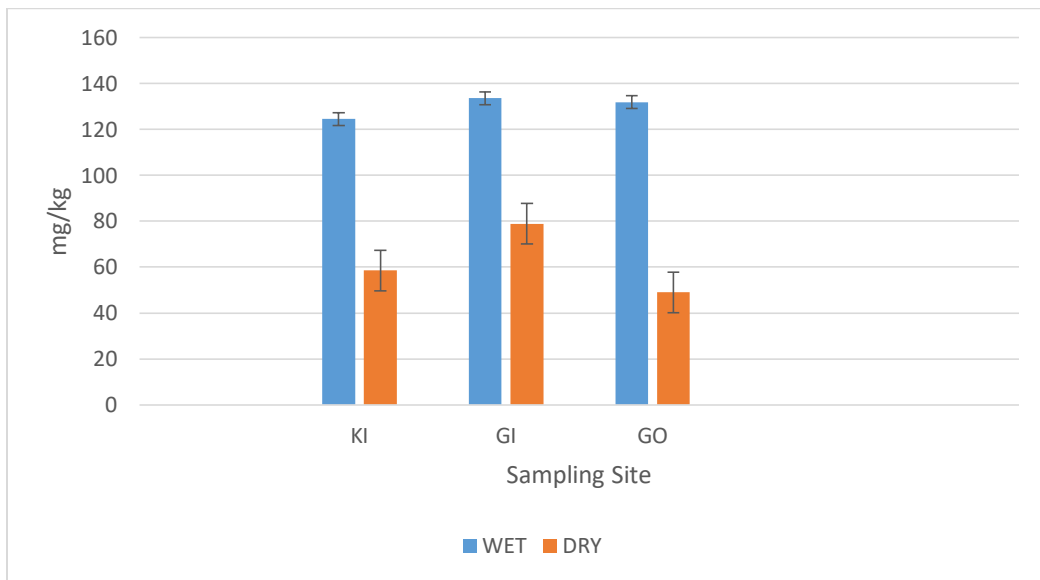


Figure 4.25b: Levels of chromium in sediment samples in selected sites dry and wet seasons.

The sediment's chromium levels varied from 49.00 ± 0.06 mg/kg – 133.57 ± 0.04 mg/kg in both season (Table 4.7) with site GI having the highest level.

In dry season, the chromium levels in sediment samples were moderately polluted according to the CCME (Ontario) and EPA sediment quality guideline except in site GI which was above the EPA guideline, while the levels of chromium in wet season indicates severe pollution of chromium

according to the compared sediment quality guidelines. This may be a result of industrial discharges into the catchment area as site GI (Githika Inlet) is located near the tea factory. Leaching from the topsoil and rocks may also be a natural source of chromium pollution.

Health effects of too much chromium include kidney damage, high blood pressure, lung cancer, and bone abnormalities like osteoporosis and osteomalacia (Pandey & Madhuri, 2014).

4.4.4 Zinc (Zn)

In the wet season, the level of zinc in water samples ranged from 0.0426 ± 0.003 mg/L – 0.1432 ± 0.020 mg/L while in dry season, zinc levels ranged from BD – 0.115 ± 0.029 (Table 4.6).

In the sediment samples, the Zn levels were detected from all the sampling sites in both the dry and wet seasons (Figure 4.26b), having levels that ranged from 12.21 ± 0.82 mg/kg - 295.38 ± 1.14 mg/kg (Table 4.7).

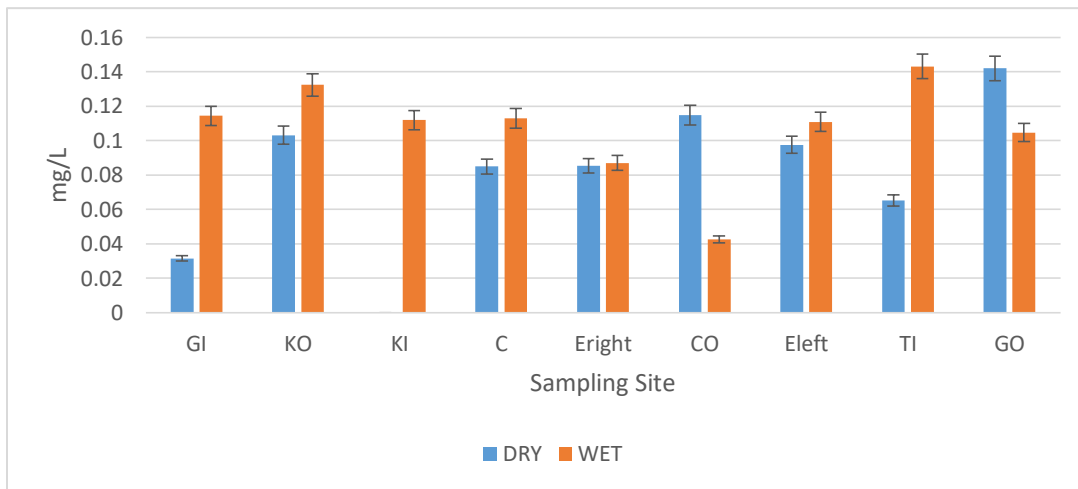


Figure 4.26a: Zn levels in water samples in selected sites in dry and wet season

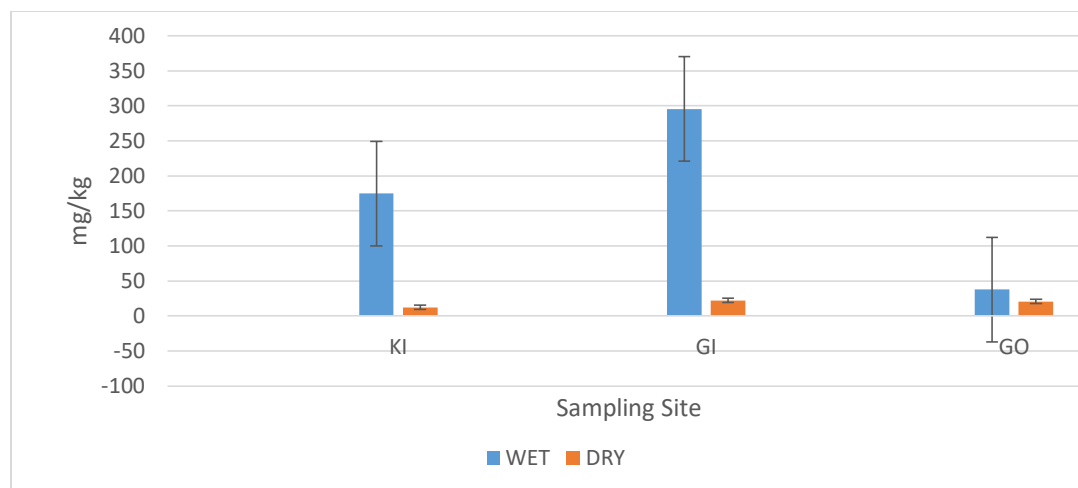


Figure 4.26b: Zn levels in sediment samples in selected sites in dry and wet season

According to studies, the earth crust naturally comprises about 0.05 g/kg of zinc (Dohare *et al.* 2014). In figure 4.26a, zinc levels were higher in wet seasons probably due to roof runoff during storm (Good, 1993). According to the author, leaching of zinc from galvanized roof surface during the storm contributes to aquatic toxicity. There is no WHO health-related recommended value for zinc in drinking water, however, imbalances in the electrolyte, vomiting, abrupt renal failures, and abdominal discomfort have been recorded as indications of high zinc exposure in humans by medical specialists (Popoola *et al.*, 2019).

The zinc levels in the sediment were below the CCME (Ontario), EPA and SLG (Ontario) sediment quality guidelines for pollution except in site KI and GI in wet season that were moderately and heavily polluted respectively.

4.4.5 Manganese (Mn)

As shown in Figure 4.27a, manganese levels in water samples in the dry season, varied from 0.1727 ± 0.008 mg/L – 0.2172 ± 0.024 mg/L while in wet season the values were from 0.2629 ± 0.026 mg/L – 0.5105 ± 0.032 (Table 4.6). Figure 4.26b shows manganese levels in sediment samples. Levels in the dry season ranged from 41.44 ± 0.89 mg/kg – 48.27 ± 15.94 mg/kg while in wet season, the concentration of manganese ranged from 53.56 ± 2.92 mg/kg – 109.25 ± 17.43 mg/kg (Table 4.7).

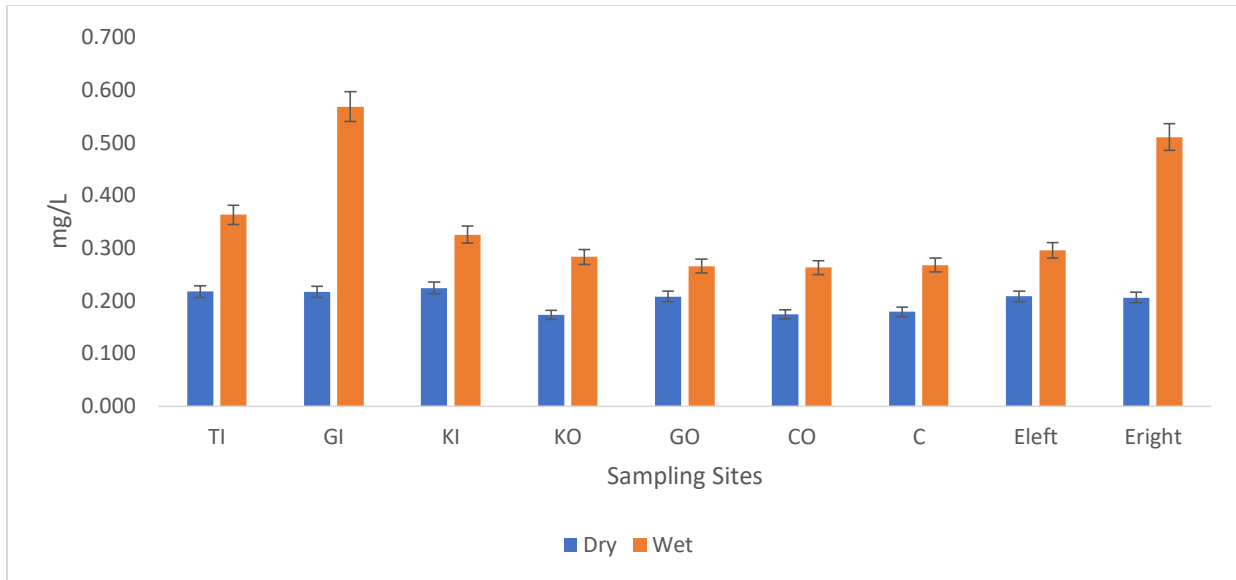


Figure 4.27a: Manganese levels in water samples in selected sites dry and wet seasons.

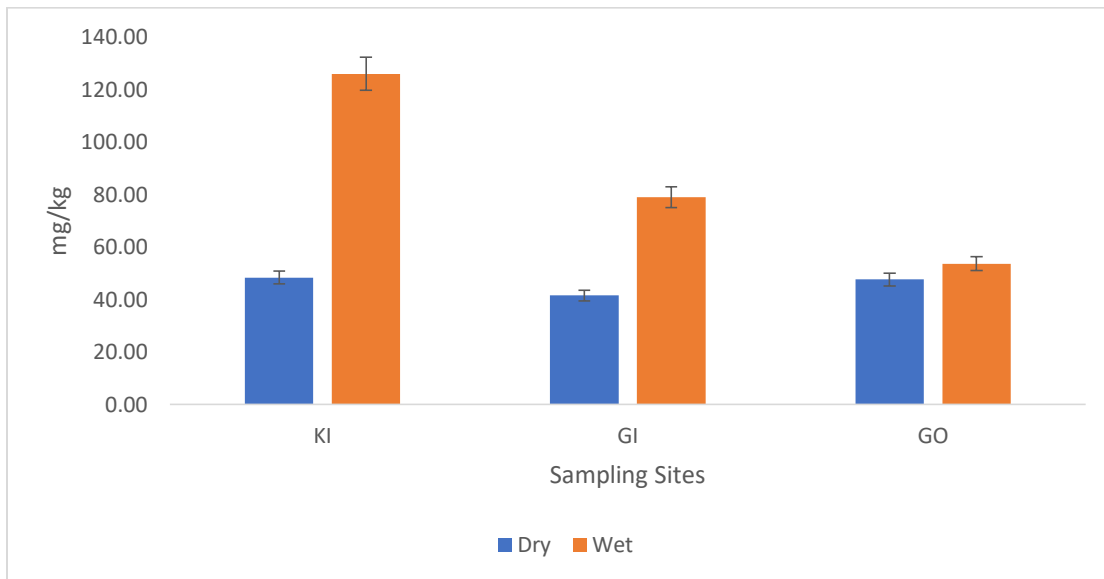


Figure 4.27b: Manganese levels in sediment samples in dry and wet seasons.

Manganese levels in all water samples in the sites were higher than the WHO's acceptability taste threshold of 0.01 mg/L by consumers (WHO, 2011) and 0.1mg/L guideline value of KEBS (2014). These could be due to dissolution of manganese-contained in the soil, rock, and minerals in the aquifer, industrial liquid waste discharged into the soil, or landfill and sewage leachate accumulated over time. High manganese levels in water cause a metallic effect as well as

unpleasant taste in the water. It also causes a blackish staining of clothes, plumbing fixtures and the creation of darkish scales in water pipes (Takeda 2003) which may lead to buildup of deposits in the distribution systems (WHO, 2011). However, no evidence of excess manganese posing a health concern in people has been found (Popoola *et al.*, 2019).

On comparison, it was found that the levels of manganese in the sediment in both seasons were below the EPA, CCME (Canada) and SLG of Ontario sediment quality guidelines.

4.4.6 Iron (Fe)

As shown in the Figure 4.28a, in the wet season, iron levels in water samples were higher than the levels in the dry season. Iron levels in wet season varied from 0.3408 ± 0.075 – 2.6643 ± 0.732 mg/L while in dry season it ranged from 0.1823 ± 0.003 mg/L – 2.401 ± 0.027 mg/L (Table 4.6).

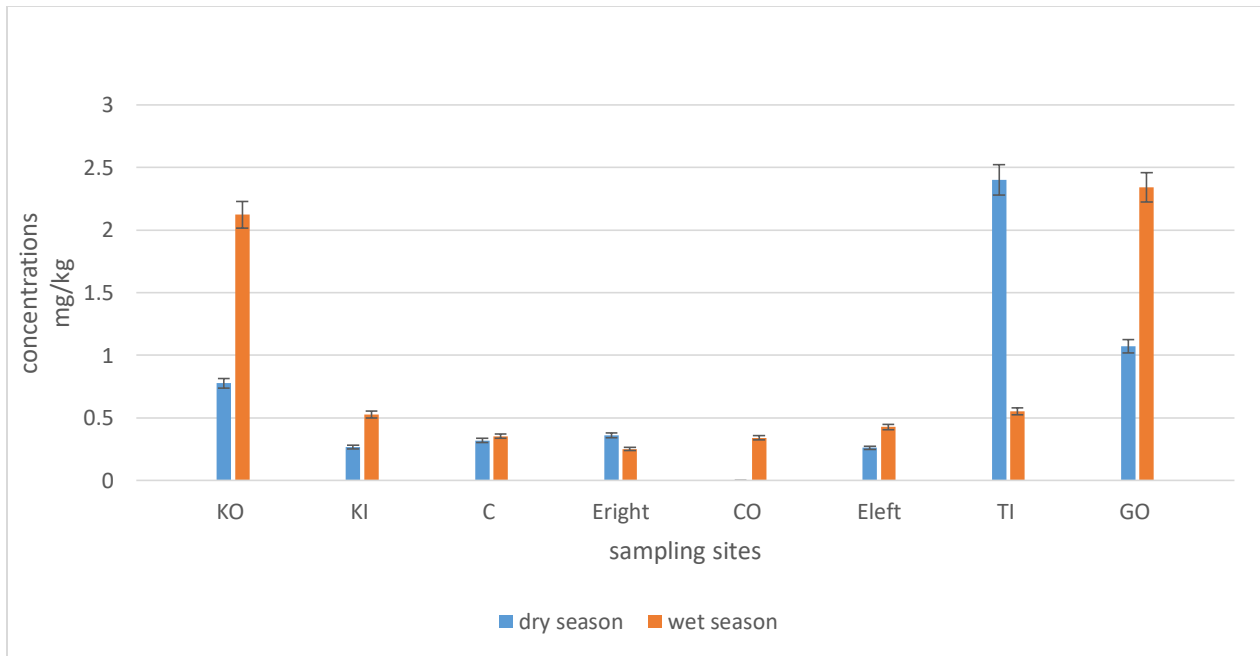


Figure 4.28a: Iron levels in water samples in selected sites in dry and wet seasons.

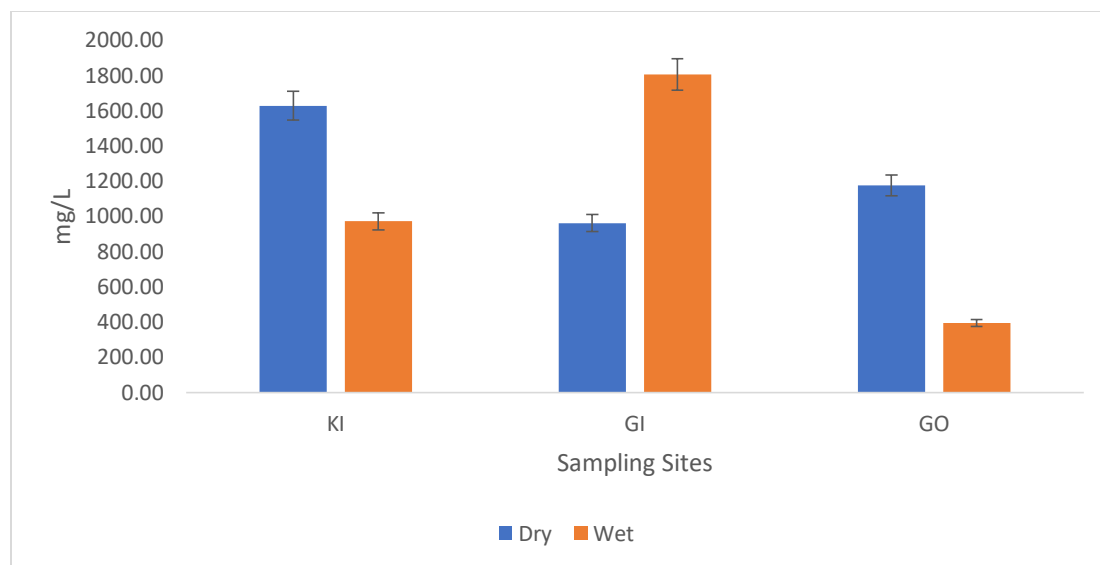


Figure 4.28b: Iron levels in sediments samples in selected sites in the dry and wet seasons.

The levels of iron in water samples exceeded the WHO (2011) and KEBS (2014) guideline limit of 0.3 mg/l for natural portable water. This is probably because of the abundance of iron in nature. Additionally, according to Neal *et al.*, 2008, it has been suggested that the increase in iron may have been driven by the increase in dissolved organic matter (DOM) since this will allow more iron to stay in the water. Striking trends of increasing iron (Fe) concentration in surface water have been reported for headwater catchment in Finland (Sarkkola *et al.*, 2013) and also in the stream of Bavaria, Germany (Knorr, 2006).

Across the study sites, during the wet season, Fe levels in sediment samples ranged from 395.53 \pm 8.90 – 1806.42 \pm 43.82 mg/kg while in dry the values were from 961.97 \pm 13.40 – 1627.98 \pm 5.90 mg/kg (Table 4.7). The highest level recorded in site GI having 1806.42 \pm 43.82 mg/kg (Figure 4.28b). The level of iron in sediment was excessively higher than the SLG (Ontario) sediment quality guideline. There is no enough literature on iron in sediment from EPA and CCME (Canada) guidelines.

4.4.7 Cadmium

The cadmium levels in the water and sediment samples from Ndakaini Dam in both dry and wet season were below the detection limit (0.001 mg/L) of AAS-flame equipment used.

4.5 Pearson Correlation Result

Pearson's correlation (r) demonstrates the existence of a relationship between two continuous variables and has values between -1 to 1. This study used Pearson's correlation as the statistical method to assess the association between pollutants in the locations under investigation. A negative number indicates a negative correlation between variables, whereas no sign indicates the correlation is positive. A value of $r = 0$ indicates that there is no significant relationship between parameters (Popoola et al., 2019). Variables are strongly correlated when r is greater than 0.7, moderately correlated when r is between 0.5 and 0.7, and weakly correlated when r is less than 0.5. (Saleem et al. 2019).

Table 4.8 presents the resulting Pearson's correlations of the physicochemical parameters. It showed 9.8% of the physiochemical parameters strongly ($r \geq 0.7$) correlated, 21.56% moderately ($0.5 < r < 0.7$) correlated, and 68.64% poorly ($r < 0.5$) correlated. At $p < 0.05$, the parameters which exhibited both positive and strong correlation with each other include: Colour with turbidity ($r = 0.944$) and TSS ($r = 0.761$); Electrical Conductivity with TDS ($r = 1.00$), and TS ($r = 0.993$) and TDS with TS ($r = 0.993$).

Table 4.8 Pearson correlation of the physicochemical properties of water samples.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1 Colour	1													
2 Temperature	-.209	1												
3 Turbidity	.944**	-.266	1											
4 Electrical Conductivity	-.106	.102	-.118	1										
5 pH	.110	-.232	.098	-.360**	1									
6 Total Dissolved Solids	-.112	.114	-.124	1.000**	-.356**	1								
7 Dissolved Oxygen	.305*	-.289*	.394**	-.079	.102	-.078	1							

8	Biological Oxygen Demand	-.285*	.344*	-.245	.215	-.650**	.218	-.030	1						
9	Chemical Oxygen Demand	-.362**	.566**	-.331*	.002	-.575**	.012	-.367**	.579**	1					
10	Total Hardness	-.018	.432**	.012	.266	-.228	.267	.219	.204	.056	1				
11	Total Alkalinity	.052	.220	.060	-.608**	-.166	-.606**	-.042	-.017	.296*	-.330*	1			
12	Total Suspended Solids	.761**	-.075	.672**	-.098	.090	-.103	.152	-.431**	-.330*	-.098	.013	1		
13	Total Solids	-.023	.108	-.045	.993**	-.343*	.993**	-.061	.165	-.029	.255	-.609**	.015	1	
14	Calcium Hardness	.377**	.551**	.393**	-.021	.219	-.031	.120	-.625**	-.523**	.146	-.056	.348**	.009	1

** = Correlation is significant at the 0.01 level; * = Correlation is significant at the 0.05 level (2-tailed). - = negative correlation

From Table 4.9 which presents the Pearson's correlation of the nutrient parameters, only NO_3^- strongly correlated with NO_2^- ($r = 0.922$). For the heavy metals (Table 4.11), Zn correlated strongly with Pb ($r = 0.844$) and Mn ($r = 0.712$).

Table 4.9: Pearson correlation values for the nutrient properties in water samples.

		1	2	3	4	5	6
1	SO_4^{2-}	1					
2	Phosphate	-.418**	1				
3	Chloride	-.194	.095	1			
4	NO_3^-	.193	.144	-.020	1		
5	Fluoride	.480**	-.527**	-.458**	.002	1	
6	NO_2^-	.041	.174	.064	.922**	-.203	1

** = Correlation is significant at the 0.01 level; * = Correlation is significant at the 0.05 level (2-tailed). - = negative correlation

Table 4.10 Pearson correlation of the heavy metal properties of water samples.

	1	2	3	4	5	6	7
Zn	1						
Si	.132	1					
Pb	.844**	.162	1				
Mn	.712**	.120	.791**	.751**	1		
Cr	-.452**	.266	-.259	-.440**	-.160	1	
Cu	.443**	-.168	.464**	.391**	.216	-.264	1

** = Correlation is significant at the 0.01 level; * = Correlation is significant at the 0.05 level (2-tailed). - = negative correlation

Table 4.11 presents the Pearson correlation between the physicochemical and nutrient properties of Ndakaini Dam. The result showed approximately 16% of the physiochemical parameters strongly ($r \geq 0.7$) correlated, 17% moderately ($0.5 < r < 0.7$) correlated, and 67% poorly ($r < 0.5$) correlated. The parameters which exhibited both positive and strong correlation with each other include: Colour with SO_4^{2-} ($r = 0.896$) and phosphate ($r = 0.783$); Turbidity with SO_4^{2-} ($r = 0.945$); EC with NO_3^- ($r = 0.965$) and NO_2^- ($r = 0.952$); TDS with NO_3^- ($r = 0.962$) and NO_2^- ($r = 0.950$); BOD with SO_4^{2-} ($r = -0.795$); COD with SO_4^{2-} ($r = -0.844$); TS with NO_3^- ($r = 0.970$) and NO_2^- ($r = 0.951$).

Table 4.11 Pearson correlation between the physicochemical and nutrient properties of Ndakaini Dam

	SO ₄ ²⁻	Phosphate	Chloride	NO ₃ ⁻	Fluoride	NO ₂ ⁻	SO ₄ ²⁻	Phosphate
NTU COLOUR	.896**	-.392**	-.288*	.089	.439**	-.051	.474**	.783**
Temperature	-.162	.144	.296*	-.044	-.664**	.195	-.652**	-.148
Turbidity	.945**	-.466**	-.272*	.084	.562**	-.069	.453**	.773**
Electrical Conductivity	-.001	.252	.055	.965**	-.180	.952**	-.226	.032
pH	.007	-.192	-.705**	-.284*	.546**	-.357**	.621**	-.299*
Total Dissolved Solids	-.007	.259	.056	.962**	-.186	.950**	-.234	.026
Dissolved Oxygen	.357**	-.270*	.036	.027	.329*	-.060	.317*	.279*
Biological Oxygen Demand	-.230	.430**	.495**	.102	-.705**	.223	-.795**	.159
Chemical Oxygen Demand	-.312*	.248	.650**	-.125	-.573**	-.013	-.844**	-.112
Total Hardness	-.120	-.096	.114	.268	.085	.190	-.007	.246
Total Alkalinity	.102	.019	.215	-.604**	-.156	-.522**	-.207	-.006
Total Suspended Solids	.621**	-.397**	-.251	.018	.300*	-.049	.462**	.628**
Total Solids	.066	.210	.023	.970**	-.150	.951**	-.179	.098
Calcium Hardness	.451**	-.427**	-.309*	.104	.639**	-.081	.664**	.053

** = Correlation is significant at the 0.01 level; * = Correlation is significant at the 0.05 level (2-tailed). - = negative correlation

Table 4.12 presents the Pearson correlation between the physicochemical and heavy metals properties of Ndakaini Dam. The result showed approximately 2% of the physicochemical parameters strongly ($r \geq 0.7$) correlated, 7% moderately ($0.5 < r < 0.7$) correlated, and 91% poorly ($r < 0.5$) correlated. The parameters which exhibited both positive and strong correlation with each other include: BOD with Pb ($r = -0.762$) and Cd ($r = -0.805$); and COD with Pb ($r = -0.714$) and Cd ($r = -0.763$).

Table 4.12 Pearson correlation between the physicochemical and heavy metals properties of Ndakaini Dam

	Pb	Cd	Mn	Cr	Cu
NTU COLOUR	.463**	.480**	.285*	.176	.007
Temperature	-.496**	-.647**	-.521**	.374**	-.288*
Turbidity	.454**	.458**	.299*	.078	-.028
Electrical Conductivity	-.125	-.217	-.155	.100	-.099
pH	.547**	.682**	.484**	-.331*	.370**
Total Dissolved Solids	-.132	-.224	-.161	.102	-.102
Dissolved Oxygen	.232	.307*	.277*	-.132	-.001
Biological Oxygen Demand	-.762**	-.805**	-.570**	.361**	-.377**
Chemical Oxygen Demand	-.714**	-.763**	-.601**	.318*	-.386**
Total Hardness	.000	.088	.183	-.235	-.126
Total Alkalinity	-.167	-.243	-.220	.276*	-.077
Total Suspended Solids	.451**	.405**	.211	.063	.000
Total Solids	-.078	-.176	-.136	.108	-.102
Calcium Hardness	.622**	.677**	.472**	-.491**	.125

** = Correlation is significant at the 0.01 level; * = Correlation is significant at the 0.05 level (2-tailed). - = negative correlation

Table 4.13 presents the Pearson correlation between the nutrient parameters and heavy metals properties of Ndakaini Dam. The result showed nearly 1% of the parameters strongly ($r \geq 0.7$) correlated, 2% moderately ($0.5 < r < 0.7$) correlated, and 97% poorly ($r < 0.5$) correlated. The

parameters which exhibited both positive and strong correlation with each other include: Zn with fluoride ($r = 0.810$); Pb with fluoride ($r = 0.753$); and Cd with fluoride ($r = 0.821$).

The remaining parameters were both positively and negatively associated, with r values of less than 0.7 indicating that they were not significantly correlated. The bulk of the parameters measured, showed association with each other at p 0.05 or 0.01, indicating that the presence of specific pollution indicators undoubtedly impacts on other contaminants in the Ndakaini Dam samples.

Table 4.13 Pearson correlation between the nutrient parameters and heavy metals of Ndakaini Dam

	SO_4^{2-}	Phosphate	Chloride	NO_3^-	Fluoride	NO_2^-
Zn	.387**	-.473**	-.566**	-.069	.810**	-.249
Si	.667**	-.144	-.053	.141	.120	.062
Pb	.378**	-.375**	-.561**	-.003	.753**	-.138
Cd	.369**	-.485**	-.527**	-.053	.821**	-.247
Mn	.179	-.368**	-.473**	-.043	.611**	-.170
Cr	.096	.335*	.167	.118	-.419**	.180
Cu	-.065	.085	-.258	-.109	.325*	-.128

** = Correlation is significant at the 0.01 level; * = Correlation is significant at the 0.05 level (2-tailed). - = negative correlation

4.6 Discussion

Human settlement at the upper reaches of the Ndakaini water catchment has led to different anthropogenic activities at different regions which may cause an alteration of the water quality. Agricultural activities like application of fertilizers in farming, domestic waste discharge and Eucalyptus tree felling are some of the activities observed in Ndakaini water catchment area. Also, lack of domestic waste treatment plants at both Thika and Muranga trading centers compounded with surface runoffs aided by tree felling in the relatively sloppy area will undoubtedly alter the

quality of water in the catchment area. Consequently, the study of pollution load and presence of heavy metals in water and sediment caused by these human activities is crucial in water quality analysis.

From the result of this research, majority of the physical and chemical parameters for all samples collected from the studied sites in Ndakaini Dam (except site GO) are within the KEBS & WHO permissible limits for drinking water. In general, the results from the physical and chemical parameters are comparable to Reddy & Parameshwar (2016) findings from Saralasar reservoir in India, which were also within the stated figures provided by global standards.

High turbidity values observed in the sites, correlated well with the levels of suspended matter. The turbidity (in wet season) and colour levels exceeded WHO standards but are within KEBS standards. Total Suspended solids (TSS) values were above WHO and KEBS recommended values during dry and wet seasons. A relatively higher dissolved mineral content was recorded along site GO than that of sites. As it was observed in the water analysis during the dry season, only chloride and nitrates were relatively higher than other nutrient parameters measured. This explains why there was a significantly higher electrical conductivity in the water in Ndakaini dam but generally, the nutrient load is within limits.

In addition, Biological Oxygen Demand and total coliform count which represents the biological quality of the water were also above the permissible threshold for WHO (2011). From the biological results in both seasons, the total coliform values in all sampling sites did not meet WHO (2011) and KEBS limits of non-detectable standard. This results for the total coliforms and E. coli testifies that the dam were slightly polluted especially at Gituru Outlet (GO) site. In addition, both the Biological Oxygen Demand (BOD) and the Chemical Oxygen Demand (COD) showed slight higher value in dry season than in wet season. The concentration of DO at sampling points throughout the wet and dry seasons can help aquatic species survive (Uddin & Jeong, 2021).

The analysis of the selected heavy metals revealed that the detected levels of Cu, Mn, Pb (dry season), Cr, Zn and Cd were below detection limits except Fe which is higher than those recommended by WHO and KEBS. Fe levels were distinctively high in this study in all the sampling sites.

Regarding the sediment samples, three (3) sampling sites: KI, GI and GO with sediment were analyzed, other sites were not within reach. According to results of this study, Iron levels were

quite high and exceeded the CCME (Ontario), EPA and SLG (Ontario) sediment quality guidelines. The natural source like weathering of rocks might be the reason for high concentration of Fe in the catchment area. Iron metal according Betancourt *et al* (2010) can deteriorate the quality of water, including infecting it with metallic odour and taste. However, further studies are needed to explain the exact main source for the presence of high Fe concentration in the catchment area.

Lastly, some of the water sources from sites in Ndakaini Dam sampled did not match the standards set by KEBS (2014) and WHO (2011) for drinking water. Hence, are not safe for drinking raw from the dam and it's tributaries without prior treatment (disinfection). Nevertheless, the water is adjudged to be safe for domestic purposes to a great extent.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Gituru Outlet (GO)

From the result of this research, majority of the physio-chemical and biological parameters of water samples recorded at site Gituru Outlet (GO) in dry season are within the KEBS & WHO permissible limits for drinking water except odour, EC, TSS, nitrates, Nitrites, total coliform and E-coli. Colour level exceeded only WHO limits but was with KEBS limit.

In wet season, odour, colour TSS, total coliform and E-coli were above the WHO and KEBS guideline value, total alkalinity and chloride levels were below detection limit while the rest of the parameters were within both guideline limits of WHO and KEBS. Turbidity levels were higher than WHO guideline limits while nitrites and BOD levels were higher than KEBS guideline limits.

Of all the sites in Ndakaini dam under study, site GO in both seasons, recorded the highest levels of odour, TDS, EC, TS, COD, BOD and E-coli while total alkalinity level was below detection.

In both season, heavy metal contents in water were above KEBS and WHO guideline values for heavy metals in drinking water except Cu, Zn, Mn and Fe. Cd was below the detection limit of 0.001mg/L. In sediment sample, the concentrations of all the heavy metals were below the CCME (Ontario), EPA and SLG (Ontario) sediment quality guidelines except Pb, Cr in wet season and Fe in both season.

Thikka Inlet (TI)

In wet season, the water quality in site Thika Inlet (KI) conformed to WHO and KEBS guideline values for all parameters except TSS, Total coliform and E-coli. Colour level also exceeded WHO's guideline value of 15 pt-co for drinking water but conformed to KEBS permissible value.

In wet season, all the water quality parameters in site TI conformed to WHO and KEBS guideline value for drinking water except colour, fluoride and total coliform levels which were higher. Turbidity levels also exceeded WHO guideline value. Phosphate and chloride levels were not detected. For TI water samples, all the parameters in the dry and wet season for heavy metals

conformed to WHO and KEBS guideline limits for drinking water except Pb, Mn and Fe. Cd and Cr were below detection level. No sediment sample was collected from site TI.

Githika Inlet (GI)

In both seasons, the odour, colour, TSS, and total coliform levels in site Githika Inlet (GI) were above the permissible value by WHO while every other physio-chemical and biological parameters conformed to KEBS and WHO guideline value. In the wet season, turbidity level was above WHO guideline value while Nitrites and BOD level was above KEBS guideline value. Chlorides level in water was below detection limit. For GI water samples, in both seasons, all the parameters for heavy metals conformed to WHO and KEBS guideline limits for drinking water except Pb, Mn and Fe. Cd and Cr were below detection level. In sediment sample, according to CCME (Ontario), EPA and SLG (Ontario) sediment quality guidelines, site GI were heavily polluted with Pb, Cr, Fe and Zn (in wet season) while Cd was below detection limit.

Kayuyu Inlet (KI)

Site Kayuyu Inlet (KI) in both season, recorded levels of odour, colour, Nitrites, total coliform, E-coli and TSS higher than the guideline limit set by WHO and KEBS while the rest of the water quality parameters adhered to the limit. However, turbidity level was only above the WHO guideline but below KEBS limit. Calcium hardness was BDL. Whereas in wet season, chloride level was BDL.

For KI water samples, all the parameters during both seasons for heavy metals conformed to WHO and KEBS guideline limits for drinking water except Pb, Cr and Fe. Cd was below the detection limit. The sediment from site KI has levels of Pb(wet season) and Cr (both season) above the CCME (Ontario), EPA and SLG (Ontario) sediment quality guidelines except Cu and Mn. According to EPA guideline, Site KI was moderately polluted with Zn.

Kiama Outlet (KO)

The water quality parameters in site Kiama Outlet (KO) during the dry season, conformed to the guideline value set by WHO and KEBS except odour, pH, TSS, nitrites and total coliform. In wet season, TSS, nitrites and total coliform did not conform to WHO and KEBS guideline standards.

In water samples, concentration of all the heavy metals under study in site KO were below detection level except Pb (in both seasons) and Fe (wet season) that had levels above WHO and KEBS guideline limits. No sediment sample collected from site KO.

Chinia Outlet (CO)

The water quality parameters in site Chania Outlet (CO) during the dry season conformed to the guideline value set by WHO and KEBS except odour, TSS, total coliform and E-coli levels. Nitrites level were higher than KEBS guideline value only. In wet dry season, all the parameters both physical chemical and biological are within the set limit by WHO and KEBS standards except colour, TSS, pH, nitrites and total coliform while turbidity level was above WHO guideline limit only. Chloride level was below detection limit.

In water sample, the result from the heavy metal contents in site GO showed that Pb, Cr and Mn (dry season) were above the KEBS and WHO guideline values for heavy metals in water while in wet season, Pb, Cr and Fe were above the guideline values. Cd was below detection.

No sediment samples was collected in Site CO.

INSIDE DAM (Site C, Eright & Eleft)

Water samples from inside Ndakaini dam itself were taken from the centre of the dam (site C) and from both edges of the dam (left edge and right edge). For site C in the dry season, the parameters conformed to the guideline limits set by WHO and KEBS standards for drinking water except pH, temperature, total coliform, Pb, Cr and Fe. In the wet season, all the other parameters conformed except TSS, temperature, total coliform, Pb and Fe.

For site Eleft in the dry season, the parameters conformed except pH, temperature, total coliform, E-coli, Pb, Cr and Fe. In the wet season, all other parameters conformed except TSS, temperature, total coliforms, Pb and Fe.

For site Eright in the dry season, the parameters conformed except pH, total coliform, temperature, Pb, Cr and Fe. In the wet season, all other parameters conformed except TSS, temperature, total coliforms and Pb.

In both season, heavy metal contents in water samples from inside the dam were above KEBS and WHO guideline limit for heavy metal in drinking water except Zn, and Cu (in wet season). Cd and Cu (dry season) was below detection. No sediment sample was collected from inside the dam.

The levels of heavy metals, overall, generally increased implying that the alteration is caused by the changing anthropogenic activities. Significantly high values of trace metals in water were registered at the agriculturally dominant areas; along sites (GI, KI and KO) and GO downstream of the dam where there are wide range of domestic activities and discharge.

According to results of this study, there is clear evidence of element of influence from Sedimentation as the sediment from three (3) out of the nine (9) sampling stations posit low to high presence of heavy metals. A worth noting point is that Iron and Manganese levels were quite high and exceeded the joint KEBS and WHO (0.3 mg/L for Iron and 0.1 mg/L for manganese) guidelines for natural potable water and drinking water (WHO, 2011). These two metals (iron & Mn) according to Betancourt *et al.*, 2010, can deteriorate the quality of water, including infecting it with metallic odour and taste. However, further studies are needed to explain the exact main source for the presence of high Mn and Fe concentration in the catchment area.

The sources of pollution in Ndakaini dam catchment may be from the anthropogenic activities carried within the catchment like agricultural activities, discharge of industrial and domestic effluents. There are tea farming and plantation of cash crop along most of the tributaries of the dam which possibly promotes run off of fertilizer pesticides and sediments from the farms into rivers during rainfall.

Effluents from the tea factories situated near some of the sampling site may be a contributory factor in alteration of the water quality of Ndakaina dam. Also, lack of adequate domestic waste treatment plants at both Thika and Muranga trading centers coupled with feaces from animal rearing around the catchment may contribute to the pollution along the tributaries of the dam.

5.2 Recommendations

The following are the recommendation from the research:

1. Further research should be done to investigate the precise source for the presence of very high Fe concentration in the catchment area.
2. Consideration of other heavy metals not included in this study such as arsenic and nickel concentrations in the water and sediments along the Ndakaini water catchment should be carried out.
3. More research should be carried out on other sites of the dam.

4. Further studies should be carried out on effect of depth on the metal concentrations in water and sediment samples within Ndakaini dam and its tributaries.
5. The levels of cadmium, copper, chromium, manganese, lead and zinc in water samples were below detection limit of AAS- flames techniques. An intending researcher to carry out analysis of the aforementioned heavy metals using ICP-MS techniques.

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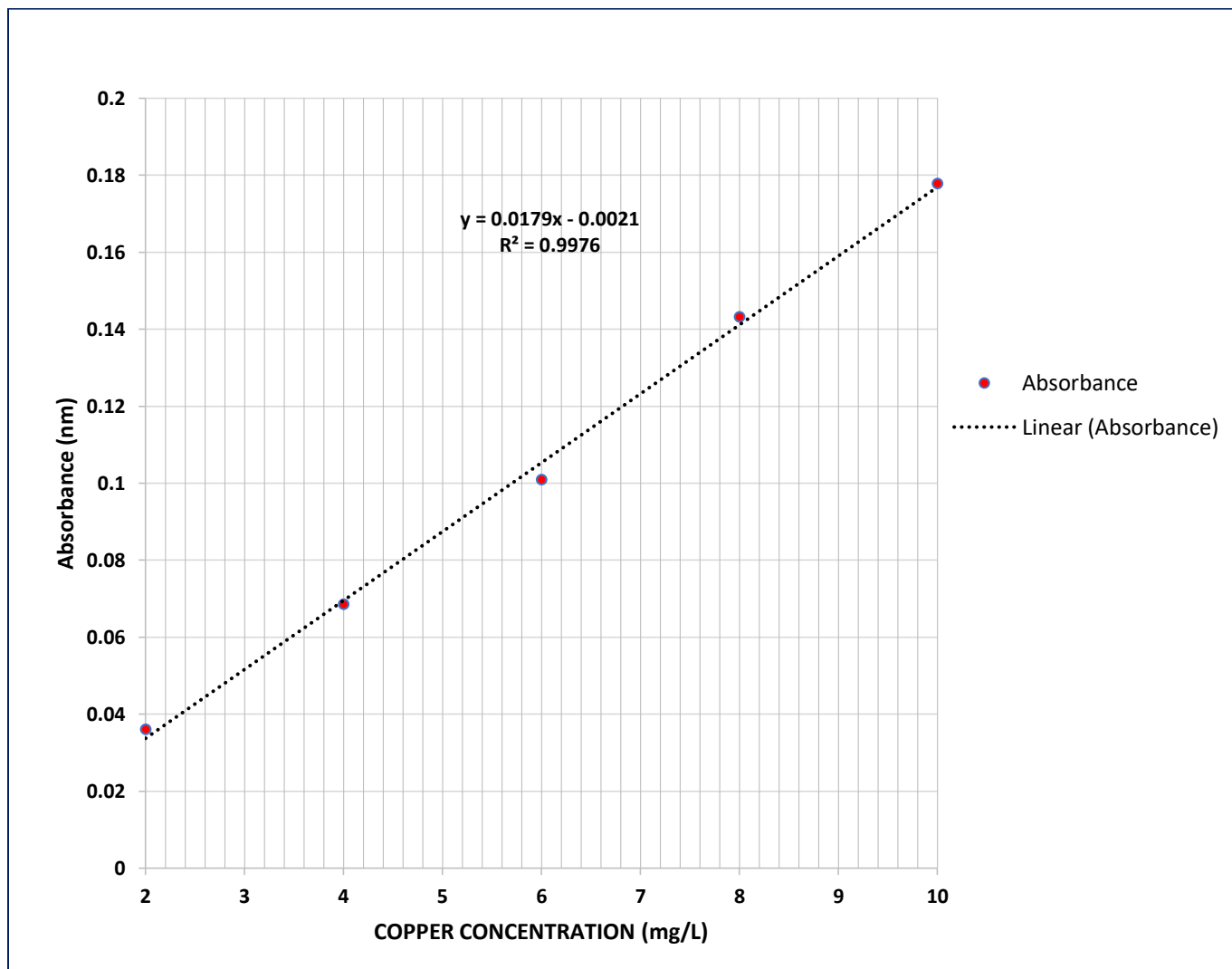
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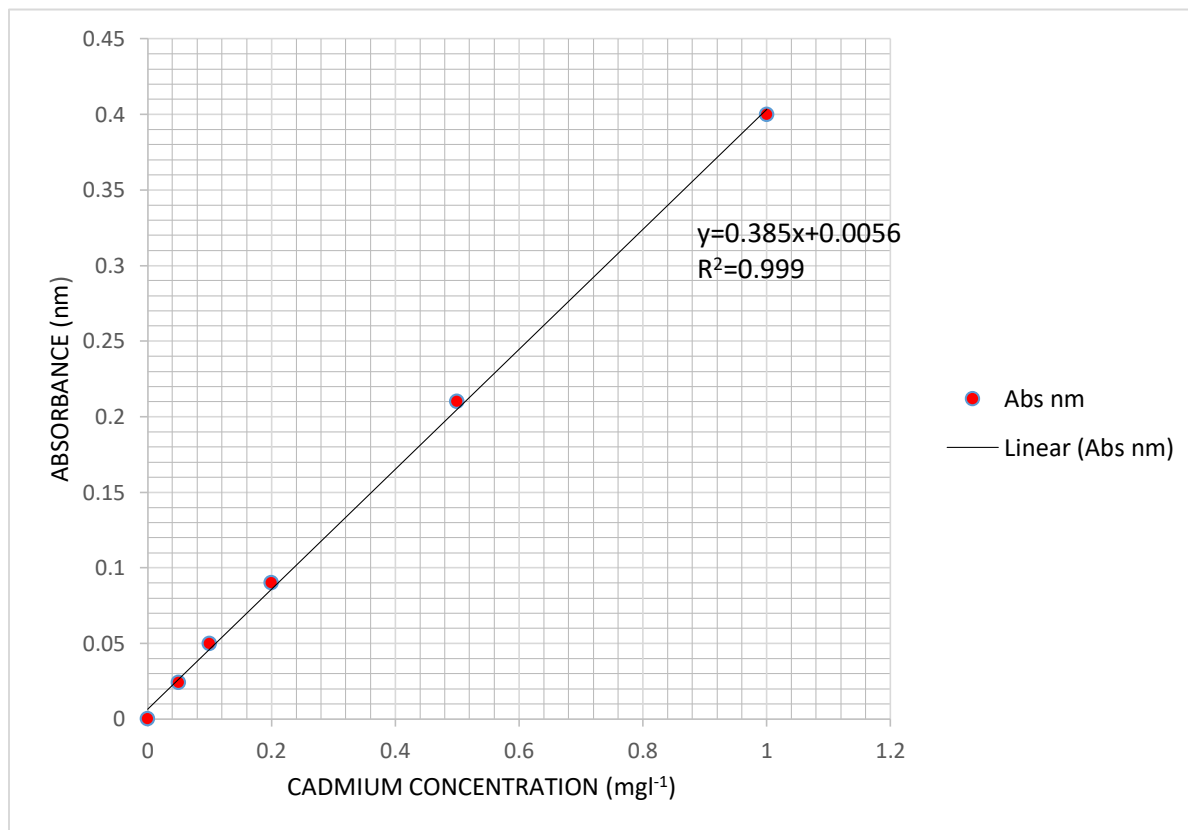
APPENDICES

Appendix 1: Calibration Standard And Curve For Cu.....	136
Appendix 2: Calibration Standard And Curve For Cd.....	137
Appendix 3: Calibration Standard And Curve For Fe	138
Appendix 4: Calibration Standard And Curve For Pb	139
Appendix 5: Calibration Standard And Curve For Mn.....	140
Appendix 6: Calibration Standard And Curve For Zn.....	141
Appendix 7: Calibration Standard And Curve For Cr	142
Appendix 8: MPN Index Table.....	143

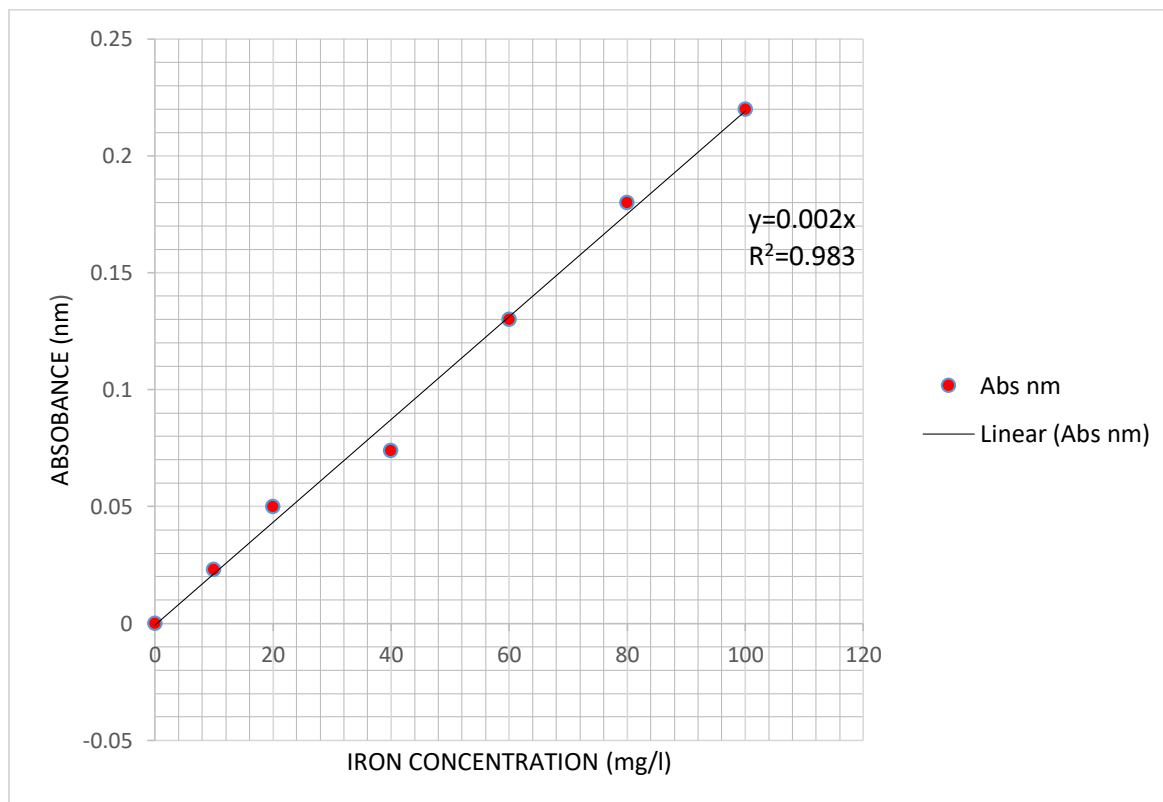
Appendix 1: Calibration Standard and Curve for Cu



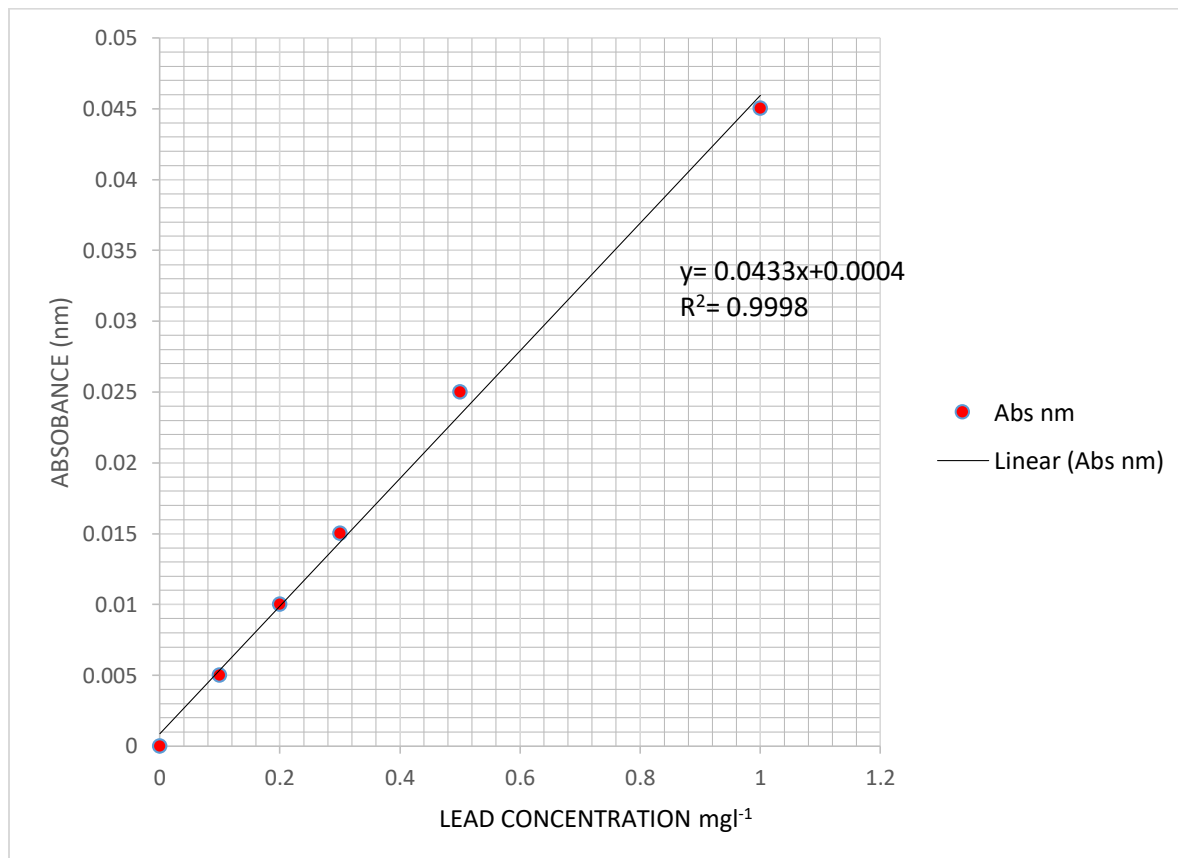
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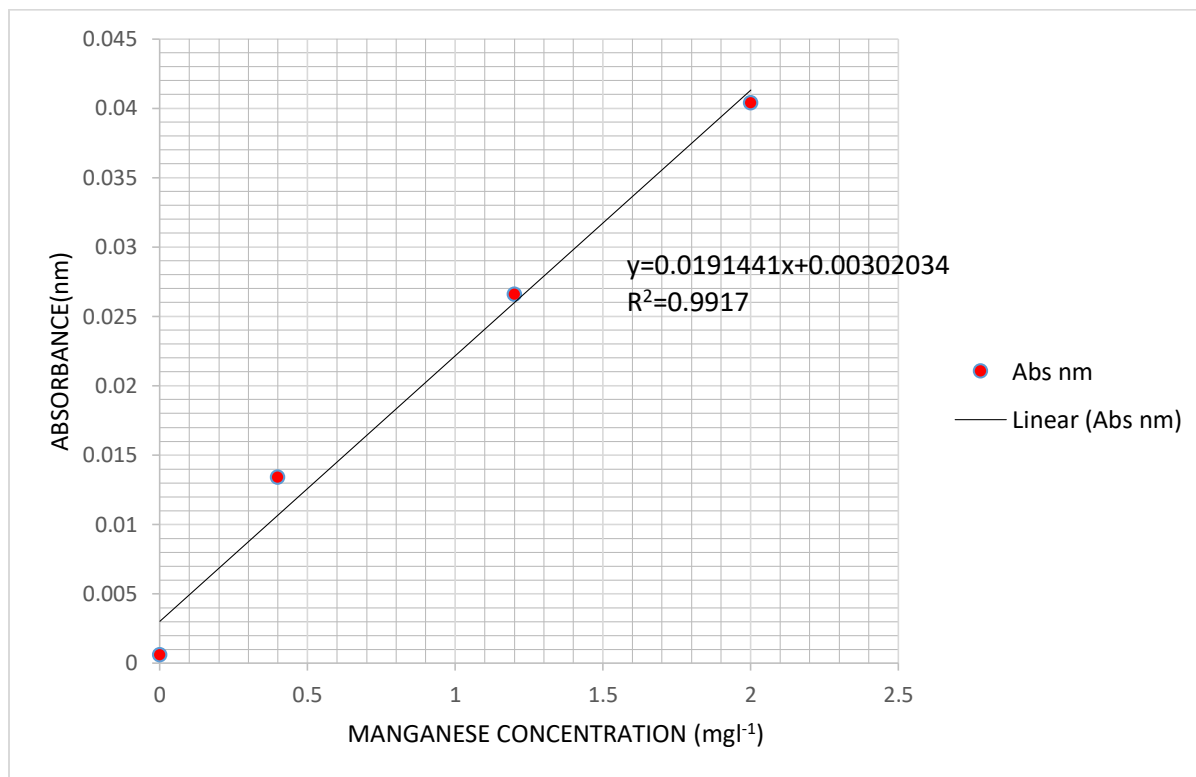
Appendix 3: Calibration Standard and Curve for Fe



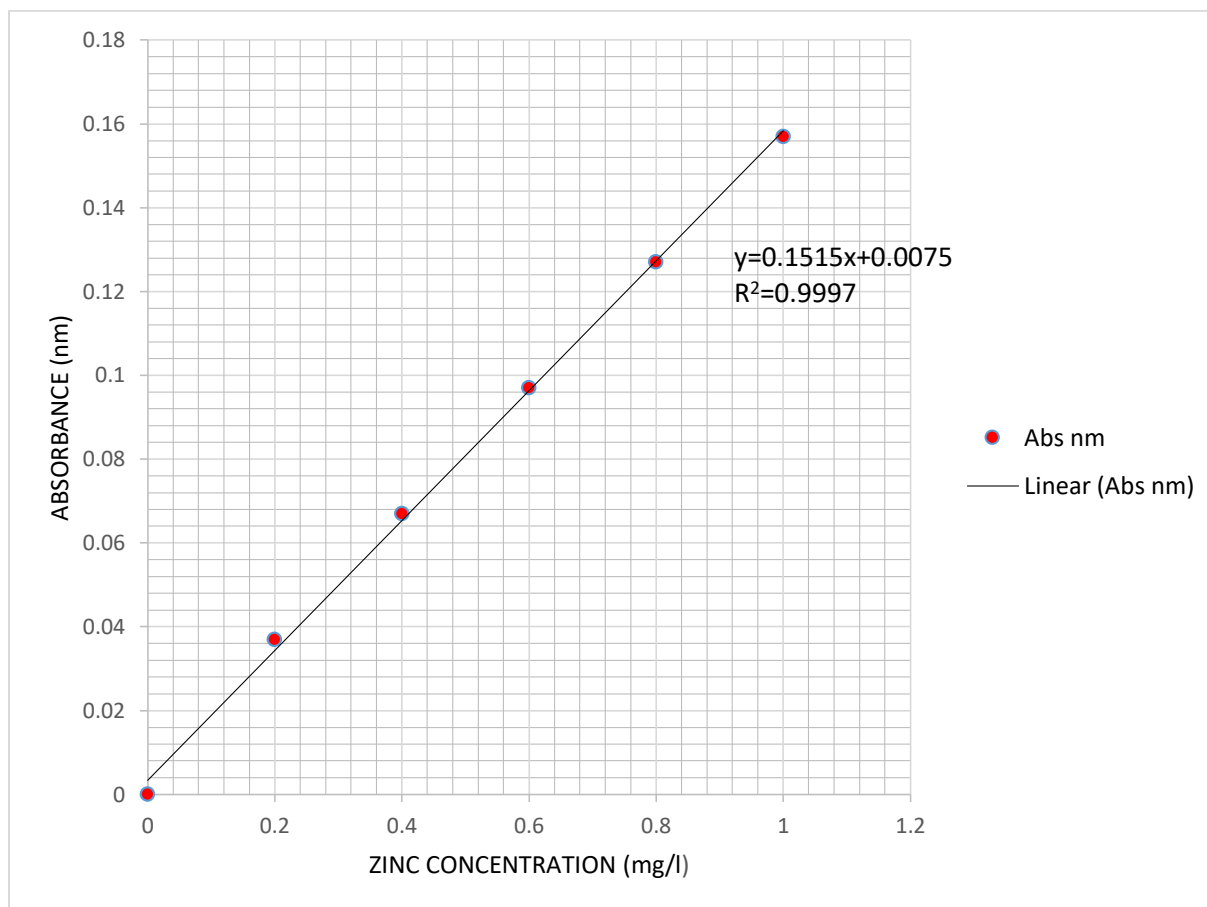
Appendix 4: Calibration Standard and Curve for Pb



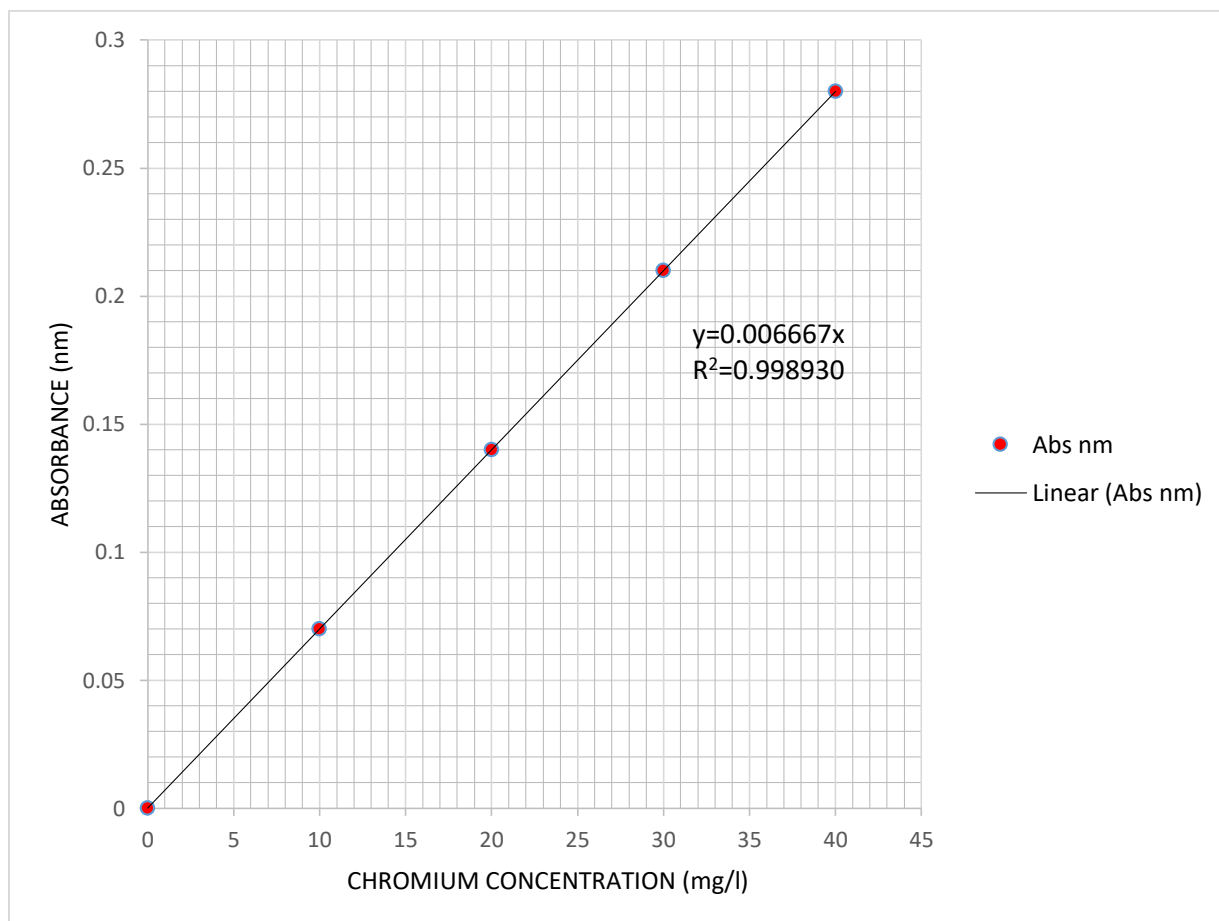
Appendix 5: Calibration Standard and Curve for Mn



Appendix 6: Calibration Standard and Curve for Zn



Appendix 7: Calibration Standard and Curve for Cr



Appendix 8: MPN Index Table

MPN index and 95% confidence limits for various combinations of positive results when five tubes are used per dilution (10 ml, 1.0 ml, 0.1 ml)

Combination of Positives	MPN Index/ 100 ml	95% Confidence Limits		Combination of Positives	MPN Index/ 100 ml	95% Confidence Limits	
		Lower	Upper			Lower	Upper
0-0-0	<2	-	-	4-2-0	22	9.0	56
0-0-1	2	1.0	10	4-2-1	26	12	65
0-1-0	2	1.0	10	4-3-0	27	12	67
0-2-0	4	1.0	13	4-3-1	33	15	77
				4-4-0	34	16	80
1-0-0	2	1.0	11	5-0-0	23	9.0	86
1-0-1	4	1.0	15	5-0-1	30	10	110
1-1-0	4	1.0	15	5-0-2	40	20	140
1-1-1	6	2.0	18	5-1-0	30	10	120
1-2-0	6	2.0	18	5-1-1	50	20	150
				5-1-2	60	30	180
2-0-0	4	1.0	17	5-2-0	50	20	170
2-0-1	7	2.0	20	5-2-1	70	30	210
2-1-0	7	2.0	21	5-2-2	90	40	250
2-1-1	9	3.0	24	5-3-0	80	30	250
2-2-0	9	3.0	25	5-3-1	110	40	300
2-3-0	12	5.0	29	5-3-2	140	60	360
3-0-0	8	3.0	24	5-3-3	170	80	410
3-0-1	11	4.0	29	5-4-0	130	50	390
3-1-0	11	4.0	29	5-4-1	170	70	480
3-1-1	14	6.0	35	5-4-2	220	100	580
3-2-0	14	6.0	35	5-4-3	280	120	690
3-2-1	17	7.0	40	5-4-4	350	160	820
4-0-0	13	5.0	38	5-5-0	240	100	940
4-0-1	17	7.0	45	5-5-1	300	100	1300
4-1-0	17	7.0	46	5-5-2	500	200	2000
4-1-1	21	9.0	55	5-5-3	900	300	2900
4-1-2	26	12	63	5-5-4	1600	600	5300
				5-5-5	≥1600	-	-