

**SURFACE WATER QUALITY ASSESSMENT IN
NG'ETHU WATER WORKS, CHANIA CATCHMENT,
KENYA**

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**Surface Water Quality Assessment in Ng'ethu Water Works, Chania
Catchment, Kenya**

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**A thesis submitted in partial fulfilment for the degree of Master of Science in
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DECLARATION

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

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DEDICATION

This research work is dedicated to God almighty for his grace and enablement. To my mother who believed in the value of education and my dear wife, Cyndi Jacinta Muthoni who stood with me in prayers and gave me moral support throughout the journey of this research work.

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LIST OF NOMENCLATURE AND ABBREVIATIONS

APHA	American Public Health Association
EC	Electrical Conductivity
FAO	Food and Agriculture Organization
KEBS	Kenya Bureau of Standards
LoD	Limit of Detection
MCL	Maximum Contaminant Level
MPN	Most Probable Number
NCC	Nairobi City County
NCWSC	Nairobi City Water & Sewerage Company
NEMA	National Environment Management Authority, Kenya
NOM	Natural Organic Matter
NTU	Nephelometric Turbidity Units
RO	Reverse Osmosis
TDS	Total Dissolved Solids
THM	Trihalomethanes
TOC	Total Organic Carbon
TSS	Total Suspended Solids
TXRF	Total X-Ray Fluorescence
USEPA	United States Environmental Protection Agency
WBDO	Waterborne Disease Outbreak
WHO	World Health Organization

ABSTRACT

Surface waters are prone to pollution especially from agriculture and other anthropogenic activities hence the need to establish its levels of contamination. This study focuses on Chania catchment situated on the lower side of the Aberdares water tower of Kenya that supplies 95% of water to the capital Nairobi. The aim of this study was to determine the physico-chemical and microbial quality of raw surface water in the catchment and after treatment during the wet and dry seasons. Grab water samples in triplicates were collected randomly from five strategic locations in pre-cleaned 500 ml plastic bottles. Analysis for heavy metals was done by Total-Reflection X-Ray Fluorescence (TXRF) Spectroscopy using S2 PICOFOX Spectrometer. TDS, EC, Turbidity, and pH were measured immediately after sampling using Portable TDS meter (3-Hm Digital), Portable EC meter (Lovibond SensoDirect Con200), Turbidimeter (HACH 2100N) and pH meter (HANNA HI 2211) respectively. Nitrates, Phosphates and Chloride ions were analysed by spectrophotometry method using UV-1800 UV-VIS Spectrophotometer. Analysis for aluminium was carried out by spectrophotometry method using HACH DR 3900 VIS spectrophotometer. Determination of Sodium was done by Flame Atomic Emission (FAES Model AA-6200 Shimadzu) Spectrophotometer. Free Residual Chlorine was determined by DPD Colorimetric method. Biological water quality analysis was done using multiple tube method according to the standard methods for the examination of Water and waste water (APHA, 2005). The raw water was found to contain a high number of microbial indicator counts during both dry and wet seasons with 1900 ± 624 MPN of Coliforms recorded at Chania River sampling point during the wet season implying that the water is not suitable for drinking without treatment. Generally, most of the physico-chemical parameters were within the allowable WHO recommended Maximum Contaminant Levels (MCL) with the exception of wet season where water samples had values of turbidity higher than WHO guideline values with the highest mean turbidity of 107.89 ± 5.85 NTU recorded at Chania River sampling point. Results of heavy metal analysis revealed that the surface water in some sampling points was polluted with Manganese, Iron, Nickel and Lead above WHO recommended levels. The highest mean concentration of Iron was 3.78 ± 0.17 mg/L recorded at Chania River sampling point during the wet season. The mean lead concentration levels at the Thika reservoir discharge and Thika River sampling points during the wet season were found to be above 0.01 mg/L which is the WHO recommended standard with the highest Lead concentration level being recorded in Thika reservoir discharge point of 0.04 ± 0.01 mg/L. The highest mean concentration of Manganese was 0.20 ± 0.03 mg/L recorded at Chania River sampling point during the wet season. There was statistically significant difference in the results for most water quality parameters assessed with $p = 0.05$ confidence level using paired T-test; for instance the concentration of Manganese in Chania river between the dry and wet seasons, where ($t_{cal} = 7.668$, $t_{tab} = 2.776$, $d.f = 4$, $P = 0.05$). The results of this study indicated that the catchment is polluted by microbial and metal pollutants, however, after treatment the microbiological quality of water was found to be within acceptable levels. It is therefore concluded that surface water within Chania Catchment is not fit for drinking

directly before treatment and that the treatment method requires improvement so as to enhance removal of iron and manganese.

CHAPTER ONE

INTRODUCTION

1.1 Background

Before water can be described as potable it has to comply with certain physical, chemical and microbiological standards which are designed to ensure that the water is palatable and safe for drinking (Tebutt, 1983). Nearly half of all people in developing countries have infections or diseases associated with inadequate water supply and sanitation (Bartram, Lewis, & Wright, 2005). It is estimated that 80 per cent of all diseases and over one third of deaths in developing countries are caused by the consumption of contaminated water, and on average as much as one tenth of each person's productive time is sacrificed to water-related diseases (UNCED, 1992). Waterborne disease outbreak (WBDO) statistics have been compiled in the United States since 1920. During 1920 to 2002, at least 1870 outbreaks were associated with drinking contaminated water, with the most recent 12-year period (1991–2002) recording an average of 22.5 per year, having 207 WBDOs and 433,947 illnesses being reported; slightly more WBDOs occurred in non-community water systems (42%) than either community (36%) or individual systems (22%) (Michael, 2006).

Source water quality is the primary driving factor in determining the level of treatment process sophistication necessary to achieve drinking water standards and goals. More degraded raw water quality can lead to higher capital costs to achieve treatment objectives, particularly as driven by the need to design for worst case water quality events. Higher operating costs can result from the advanced treatment processes themselves and or water quality related operational issues, such as decreased filter run times, higher chemical dosing requirements, increased residual disposal costs, and frequent process adjustments due to higher water quality variability (Hudak, 2013).

Agriculture is the single largest user of freshwater resources, using a global average of 70% of all surface water supplies. It is also a cause of water pollution through its discharge

of pollutants and sediment to surface and/or groundwater, through net loss of soil by poor agricultural practices, and through salinization and waterlogging of irrigated land (FAO, 1993). Agriculture has allowed more plants and animal production per unit area of land; all this has been achieved with the application of chemicals such as fertilizers, herbicides and pesticides which have harmful effects on the environment (Ecobichon, 1996). Many other agricultural activities such as dairy farming, livestock farming, fish farming, tree and vine crop processing industries, animal slaughtering and operation of feedlots has generated a lot of uncontrollable waste (Beard *et al.*, 2014). Most farmers in developing world are not aware of the negative environmental impacts of using agro-chemicals on their farms (Jeyaratnam, 1990).

Kenya is classified by the United Nations as a chronically water-scarce country with an annual freshwater supply of about 647 m³ per capita, which is significantly below the 1000 m³ per capita set as the marker for water scarcity (Mogaka, Gichere, Davis & Hirji, 2005). The same is characterized by high spatial and temporal variability and extremes of drought and floods. Catchment degradation is a major problem, which is undermining the limited sustainable water resources base in the country. The main causes of catchment degradation are poor farming methods, population pressure and deforestation (KNWDR, 2006).

According to Nairobi City Water and Sewerage Company Limited strategic plan 2014/15 – 2018/19, Ng'ethu Water Works supplies water to Nairobi City County (NCC) and accounts for about 450,000 m³/day (85%) of all potable water supplied to the city (NCWSC, 2014). Raw water is abstracted from Chania, Kiama and Kimakia rivers. If the amount abstracted meets the water treatment plant demand, then Thika reservoir is left to re-charge otherwise the reservoir only supplies water during the dry season when river water levels are low. Ng'ethu Water Treatment Plant is a conventional water treatment that utilizes the sequential use of coagulation, flocculation, sedimentation, filtration, and disinfection (with chlorine gas). The water filtration is by rapid gravity sand filtration which is mechanical and does not employ adsorptive media such as use of powdered activated carbon (PAC) or granular activated carbon (GAC) as part of filter media at any

stage. Currently there are no technologies for the removal of nitrates and phosphates employed during water treatment at Ng'ethu Water Treatment Plant.

The source basin is the Upper Tana catchment which is situated North-West of Nairobi and covers Mount Kenya and the Aberdares highlands and generally the area has a bimodal rainfall pattern as a result of the inter-tropical convergence zone (Wilschut, 2010). The two distinct rain seasons appear fairly well distributed in the months of March to June and September to December. The rainfall is strongly influenced by orographic effects (Saenyi, 2002). On average, the area receives about 600 mm in the east to 2,000 mm of rain in the humid western boundary and the maximum and minimum mean annual temperature varies between 25.5 – 31.0 °C and 21.0 – 24.0 °C respectively (Mutua and Klik, 2007).

The Chania sub-catchment traverses the Counties of Marang'a and Kiambu. It is characterized by steep hillsides and areas of wetlands that have been converted to agriculture. This removes barriers where runoff water and sediment would be stored and filtered naturally. As a result, runoff and sediments flow into rivers and reservoirs causing serious siltation that then increases the costs for water treatment. Today, 60% of Nairobi's residents are water insecure and the challenges to water security will likely grow as climate change brings increasingly unpredictable rainfall (TNC, 2015).

1.2 Statement of the problem

There is limited information about the microbiological and physico-chemical quality of surface water sources from Chania catchment. The availability of good quality water is an indispensable feature for quality of life and preventing diseases. There are widespread anthropogenic activities along Chania sub-catchment that contribute to pollution. This catchment is largely made up of agricultural land with coffee, tea, maize and livestock keeping. The farms have sloppy landscapes especially those bordering the rivers and there is little observed riparian protection. This poses serious threat in relation to sediment flow from agricultural land into the rivers and microbial pollution of the water. There are many households within Chania catchment who fetch water directly from the rivers for domestic

use and household-level treatment methods if any may not be sufficient. Consumption of water obtained directly from the water bodies without treatment poses serious health impacts to consumers. Ng'ethu water works is a conventional water treatment plant supplied directly with surface water from Chania catchment and employs the sequential use of coagulation, flocculation, sedimentation, filtration, and disinfection (with chlorine gas). There is minimal aeration of raw water as a way of pre-treatment and no other technologies for the removal of pollutants are employed in this water works.

1.3 Justification and significance of the study

The cost of water treatment due to deterioration of raw water quality represents an important component of the societal costs of water pollution. Catchment degradation leading to pollutants flow into water courses is one such major driver that can undermine sustainability of the limited water resources.

Surface waters are prone to pollution especially from agriculture and other anthropogenic activities hence the need to establish the levels of pollution in Chania catchment. It is also necessary to assess the effectiveness of conventional water treatment process applied to remove pollutants as continued consumption of contaminated water may have adverse human health impacts hence the need for early warning. This study is aimed at establishing the quality of source water and the effectiveness of the treatment method applied at Ng'ethu Water Works with a view to recommend improvements if need be.

1.4 Hypothesis

Null hypothesis (H_0) – levels of Physico-Chemical parameters and Total Coliforms in Chania River are not affected by seasonal variations.

1.5 Objectives

1.5.1 Main Objective

To assess the water Quality parameters in Chania Catchment.

1.5.2 Specific objectives;

- i. To determine the physico - chemical quality of water in Chania River and Thika River during the dry season and wet season.
- ii. To assess the physico - chemical quality of water in Thika Reservoir during the dry and wet season.
- iii. To assess the population of Total Coliform bacteria in the raw from Chania River, Thika River, Thika Reservoir and treated water during the dry and wet season.

1.6 Study scope

This study utilized primary data from experimental analysis to examine the present levels of Total Coliform bacteria and the following Physico-Chemical pollutants;

Physico – chemical parameters to be analyzed are; Lead, Copper, Zinc, Iron, Manganese, Chromium, Aluminium, nitrates, phosphates, pH, Turbidity, Colour, and Total Dissolved Solids.

The area of interest is Chania catchment which is drained by River Chania which enters the catchment at Ragia location in Nyandarua South District flowing downstream to the confluence of Thika and Chania rivers behind Blue Post Hotel. It covers an approximate distance of 50 Km, and area of 750 km². Data for this study was collected in 2015 during both the dry season of July - September and wet season of October - December.

1.7 Theoretical Framework

The surface water sources and catchment involved in this study are hypothesized to be polluted by contaminants resulting from both human activities especially from agriculture and natural geo-chemical processes such as weathering of rocks. The pollutants may be in the form of heavy metals, ions, physical pollutants and micro-organisms that are likely to find their way into the rivers through run off and enter water treatment works after abstraction. At the treatment plant, the goal is to remove present pollutants and make the water fit for human consumption. After treatment the water flows into a clear well then is transmitted to the distribution network and to households in Nairobi County. The water is

distributed to the house holds for domestic use and if the treatment method was not effective to reduce different pollutants to acceptable levels, consumption of this water by the public poses a serious health concern. This is due to the fact that toxic substances and pathogens may be ingested and accumulate in human biological systems leading to diseases. Therefore, to ensure good quality of drinking water, the treatment method employed should be effective and also the sources of pollutants that may enter the water bodies should be identified and measures taken to prevent or control pollution.

CHAPTER TWO

LITERATURE REVIEW

2.1 General overview

Safe drinking-water is a basic need for human development, health and well-being and because of this it is an internationally accepted human right (WHO, 2010). The total volume of water on earth is about 1400 million km³ with approximately 97.5% of this volume in the oceans and seas and the remaining 2.5% (35 million km³) in fresh water (UNEP, 2002).

The greater portion of freshwater (around 69%) is in the form of ice and permanent snow cover in the Antarctic, the Arctic and in the mountainous regions of which the usable portion of these sources is only about 200 000 km³ of water - less than 1 per cent of all freshwater and only 0.01 per cent of all water on Earth (UNEP, 2002). Much of this available water is located far from human populations, thus complicating issues of water use. Only about 0.3% of the total amount of fresh water on the earth is concentrated in lakes, rivers, soil moisture and relatively shallow groundwater basins where it is most easily accessible for economic needs and extremely vital for water ecosystems (UNEP, 2002).

According to People Action International (PAI, 1997), water is the source of life and development on earth. Life is tied to water, air and food, while food is tied to water. Water is a regional resource, but water shortage is becoming a global issue due to increasing population, economic growth and climate change. Gleick (2000) indicates that there are five major drivers demanding a huge expansion of water resources in the 20th century: population growth, industrial development, expansion of irrigated agriculture, massive urbanization and rising standards of living.

Generally, there are two classes of solutions for water problems: increasing the supply of water (developing new resources) and/or decreasing the demand for water (managing available resources). According to Loucks (2000) everyone involved in water management and development has an obligation to assure that these systems should

provide sufficient quantities and qualities of water at acceptable prices and reliabilities, while protecting the environment and preserving the biodiversity.

Water pollution is a new problem approaching crisis levels in many parts of the world. Polluted water is a major cause of death and disease in the developing world. According to Love (1999) an estimated 80% of all diseases and over third of deaths in developing countries are caused by the consumption of contaminated water. Water-related diseases cause a 10% reduction in overall production effect.

The adoption of drinking-water standards that are too stringent could limit the availability of water supplies that meet those standards - a significant consideration in regions of water shortage. The standards that individual countries will develop can thus be influenced by national priorities and economic factors (WHO, 1996).

Many parameters must be taken into consideration in the assessment of water quality, such as source protection, treatment efficiency and reliability, and protection of the distribution network (e.g., corrosion control). The costs associated with water quality surveillance and control must also be carefully evaluated before developing national standards. Guideline values are not set at concentrations lower than the detection limits achievable under routine laboratory operating conditions. Moreover, guideline values are recommended only when control techniques are available to remove or reduce the concentration of the contaminant to the desired level (WHO, 1996).

2.2 Water Pollution

Water pollution means introducing any matter into waters which changes the physical, chemical or biological condition of that water (Ongley, 1996).

The quality of a stream or river is often a good indication of the way of life within a community through which it flows. It is an indicator of the socio-economic conditions and environmental awareness and attitude of its users. Everything that happens in a catchment area is reflected in the quality of the water that flows through it, because the results of human activity and lifestyle ultimately end up in rivers, through runoff (Rand Water Foundation, 2013).

Point source water pollution comes from a discrete source, such as a pipe or drain flowing from an industrial activity. Point source pollution can be critical to the health of a waterway as it occurs independently of flow conditions and can therefore impact a waterway when it has the least ability to accommodate the pollution, especially in dry conditions. Diffuse source water pollution arises from a multitude of diverse urban and rural land uses across a catchment, rather than a discrete point source. Diffuse source water pollution is mainly driven by rainfall runoff, particularly from storms, although contamination of underground water systems and aquifers can occur over long periods independently of rainfall and may be linked to current or past land uses on the ground (Ongley, 1996)

Almost all water in its natural state is impure, because of common naturally occurring and anthropogenic sources of pollution. Naturally occurring sources of pollution arise from the diversity of aquatic animals and plants that inhabit the bodies of water used eventually for human consumption. In addition to microbial organisms that live in water, fish, aquatic animals and wildlife produce wastes that contaminate the water. Soils in contact with the water also harbor microorganisms. Decaying vegetative matter contribute a lot of organic materials which affect the quality of water. Natural rock and soil formations may introduce radionuclides, nitrogen compounds, and heavy metals such as arsenic, cadmium, chromium, lead and selenium as well as other chemicals. Run-off from urban streets is a growing contributor to water pollution, especially after heavy rainfall. Pet wastes that washed into storm drains can represent a hazard to human and animal health (Robert, 2012).

2.3 Microbial Contamination

Microbial contamination of water includes bacterial, viral, protozoan or other biological pollution (WHO, 2011). The main cause of bacteriological pollution in water is caused by the excreta of warm blooded animals including man, domestic and wild animals, and birds. The main ones are Coliform group, some subgroups of faecal streptococci and other lower life form organisms. These cause a variety of diseases such as dysentery, typhoid fever,

cholera and gastroenteritis. Pollution is also brought about by alga, diatoms and small animals like protozoa, rotifers and crustaceans (Varshney, 2008). For microbial quality, verification is based on the analysis of faecal indicator micro-organisms, with the organism of choice being *Escherichia coli* or thermotolerant coliforms. *Escherichia coli* provide conclusive evidence of recent faecal pollution and should not be present in drinking water (WHO, 2011).

2.3.1 Coliform Bacteria

Coliform bacteria are organisms that are present in the environment and in the faeces of all warm-blooded animals and humans. Coliform bacteria will not likely cause illness. However, their presence in drinking water indicates that disease-causing organisms (pathogens) could be in that water system. Therefore, water sources must be protected from contamination by human and animal waste, which can contain a variety of bacterial, viral, and protozoan pathogens and helminth parasites. Failure to provide adequate protection and effective treatment will expose the consumers to the risk of outbreaks of intestinal and other infectious diseases. Those that are at greatest risk of waterborne disease are infants and young children, people who are debilitated or living under unsanitary conditions, the sick, and the elderly. For these people, infective doses are significantly lower than for the general adult population. Microbial risk can never be entirely eliminated, because the diseases that are waterborne may also be transmitted by person-to-person contact, aerosols, and food intake; thus, a reservoir of cases and carriers is maintained. Provision of a safe water supply in these circumstances will reduce the chances of spread by these other routes (WHO, 1996).

Faecal coliforms are quite specific to the feces of warm-blooded animals and *Escherichia coli* are even more specific, whereas total coliforms have many non-faecal sources (e.g. soils, plants), and thus are less indicative of faecal contamination. Coliforms generally do not survive long in cold, fresh water (Brettar, 1992), but can survive for prolonged periods in stream sediment, soils or faecal material, when associated with particulate matter, or in warmer water (Howell, Coyne, & Cornelius, 1996). Disturbance of these sediments can

therefore result in coliforms appearing in overlying water for extended periods (Jawson, Elliot, Saxton, & Fortier, 1982). These include a wide range of aerobic and facultative anaerobic, gram-negative, non-spore-forming bacilli, capable of growing in the presence of relatively high concentrations of bile salts with the fermentation of lactose and production of acid or aldehyde within 24 hours at 35 - 37°C. *Escherichia Coli* and thermotolerant coliforms are a subset of the total coliform group that can ferment lactose at higher temperatures. Total coliform bacteria occur in both sewage and natural waters. Some of these bacteria are excreted human and animal faeces, and are able to multiply in water and soil environments (WHO, 2011). Total coliforms can also survive and grow in water distribution systems, particularly in the presence of biofilms. Total coliforms should be absent immediately after disinfection, and the presence of these organisms indicates inadequate treatment. The presence of Total Coliforms in distribution systems and stored water supplies can reveal re-growth and possible biofilm formation or contamination through ingress of foreign materials. Total coliform bacteria that are able to ferment lactose at 44 - 45°C and are known as thermotolerant coliforms. In most waters, the predominant genus is *Escherichia*, but some types of *Citrobacter*, *Klebsiella* and *Enterobacter* are also thermotolerant. *Escherichia coli* is present in very high numbers in human and animal feces and is rarely found in the absence of faecal pollution, although there is some evidence for growth in tropical soils (WHO, 2011).

Since it is difficult, time-consuming, and expensive to test directly for the presence of a large variety of pathogens, water is usually tested for coliforms. Sources of faecal contamination to surface waters include wastewater treatment plants, on-site septic systems, domestic and wild animal manure, and storm runoff. The most commonly tested fecal bacteria indicators are total coliforms, fecal coliforms, *Escherichia coli*, *fecal streptococci*, and *enterococci*. All but *Escherichia coli* are composed of a number of species of bacteria that share common characteristics such as shape, habitat, or behavior; *E. coli* is a single species in the faecal coliform group. Sampling and equipment considerations are important when sampling bacteria. Natural bacteria levels in streams can vary significantly; bacteria conditions are strongly correlated with rainfall, and thus

comparing wet and dry weather bacteria data can be a problem. Many analytical methods have a low level of precision yet can be quite complex; and absolutely sterile conditions are required to collect and handle samples. It is critical when monitoring bacteria that all containers and surfaces with which the sample will come into contact with are sterile. Containers made of either some form of plastic or Pyrex glass are acceptable. Samples for bacteria must be analyzed within 6 hours of collection. Bacterial samples should be kept at freezing temperatures and then transported to the lab for analysis as soon as possible (USEPA, 1985).

2.4 Chemical Contamination

Despite the fact that microbial hazards make the largest contribution to waterborne disease in developed and developing countries, chemicals in water supplies can also cause serious health problems – whether the chemicals are naturally occurring or derive from sources of pollution (WHO, 2008). At a global scale, fluoride and arsenic are the most significant chemical pollutants, each affecting perhaps millions of people. However, many other chemicals are also important contaminants of drinking-water under specific local conditions (WHO, 2008).

Chemicals enter the water supply from natural and anthropogenic sources and reach distribution systems of drinking water supplies from various sources, including municipal and industrial discharges as well as urban and rural runoff and natural geological formations. Chemical contaminants for which epidemiologic studies have reported associations include the following: aluminium, arsenic, disinfection by-products, fluoride, lead, pesticides and radon. Health effects reported have included various forms of cancers, adverse reproductive outcomes, cardiovascular disease and neurological disease (Robert, 2012).

The health concerns associated with chemical constituents of drinking water differ from those associated with microbial contamination and arise primarily from the ability of chemical constituents to cause adverse health effects after prolonged periods of exposure. Guideline values are derived for many chemical constituents of drinking water which

normally represents the concentration of a constituent that do not result in any significant risk to health over a lifetime of consumption (WHO, 2011).

2.4.1 Heavy Metals in Surface Water

Land and water pollution by heavy metals is a worldwide issue. All countries have been affected, though the area and severity of pollution vary enormously (McGrath *et al.*, 2001). Heavy metals like copper, zinc, manganese, iron, cadmium, chromium and lead among others are usually present in water at low concentration. Enhanced concentrations of these metals have been found as a result of human activities. Water quality studies have been made in different countries by different researchers on the extent of heavy metals pollution in surface water (Zakir *et al.*, 2011).

The major sources of lead contamination of the aquatic environment are the industrial discharges from smelters, battery manufacturing units, run off from contaminated land areas, atmospheric fallout and sewage effluents. Of the atmospheric sources, combustion of leaded fuel produced maximum release of lead into the air, which resulted in higher lead levels in urban air as well as roadsides. Lead being a heavy metal inhibits the function of certain enzymes necessary for the formation in bone marrow haem, the pigment that combines with protein to form haemoglobin (Michael, 1980). Lead poisoning in children can produce brain damage (Varshney, 2008).

Chromium is widely used in a variety of industries like electroplating, tanning, manufacture of paints and pigments and fungicides (WHO, 2011). Chromium is toxic in high concentrations to both plants and animals. It is reported to cause perforations, bronchiogenic carcinoma in continuously exposed humans (Varshney, 2008).

Iron is an essential element in human nutrition. Estimates of the minimum daily requirement for iron depend on age, sex, physiological status, and iron bioavailability and range from about 10 to 50 mg/day. As a precaution against storage of excessive iron in the body, the established provisional maximum tolerable daily intake of 0.8 mg/kg of body weight which applies to iron from all sources except for iron oxides used as colouring agents, and iron supplements taken during pregnancy and lactation or for specific clinical

requirements. Allocation of 10% of this provisional maximum tolerable daily intake to drinking-water gives a value of about 2 mg/L, which does not present a hazard to health. WHO has no proposed health-based guideline value for iron (WHO, 1996). Copper mining and metallurgical operations contribute to contaminations of aquatic environments. Copper salts are used as fungicides and algicides. Bordeaux mixture, a formulation of copper sulphate and calcium carbonate is still used as a fungicide. Copper is toxic to many aquatic plants at low levels (Varshney, 2008).

2.4.2 Sodium

The sodium ion is ubiquitous in water. Most water supplies contain less than 20 mg of sodium per litre, but in some countries levels can exceed 250 mg/L. Sodium may affect the taste of drinking-water at levels above about 200 mg/L (WHO, 1996).

2.4.3 Atmospheric gases

When the concentration of soluble gases like nitrogen oxides, sulphur dioxide, hydrogen sulphide, carbon monoxide, hydrogen and ammonia increases sufficiently in the atmosphere, it subsequently enhances their content in water. However, the actual concentration of these gases in water depends upon their concentration in the atmosphere, solubility and diffusivity, temperature and viscosity of water. Generally, surface waters near the cities and industrial complexes where atmosphere is more polluted by factory smoke and discharge of burnt fuel from the vehicles are more polluted than those of rural areas (Varshney, 2008). Atmospheric emissions, mainly those containing sulphur and nitrogen oxides from fossil-fuel combustion, are the primary cause of acid rain and, consequently, acidified fresh water. Once in the atmosphere, sulphur and nitrogen are oxidized and then react with atmospheric moisture to form acids. They are then returned to Earth through wet (rain, mist, fog, snow) or dry deposition, gradually decreasing the pH of water (UNEP, 2002).

2.4.4 Electrical conductivity (EC).

Conductivity is a measure of the ability of water to conduct an electrical current. Conductivity in water is affected by the presence of inorganic dissolved solids such as

chloride, nitrate, sulfate, and phosphate anions (ions that carry a negative charge) or sodium, magnesium, calcium, iron, and aluminum cations (ions that carry a positive charge) (EPA, 2012). Organic compounds like oil, phenol, alcohol, and sugar do not conduct electrical current very well and therefore have a low conductivity when in water. Conductivity is also affected by temperature: the warmer the water, the higher the conductivity. For this reason, conductivity is reported as conductivity at 25 degrees Celsius (EPA, 2012). Conductivity is measured in micromhos per centimeter ($\mu\text{mhos/cm}$) or microSiemens per centimeter ($\mu\text{S/cm}$). Distilled water has a conductivity in the range of 0.5 to 3 $\mu\text{mhos/cm}$ (APHA, 1992).

2.4.5 Total Dissolved Solids (TDS)

TDS is the term used to describe the inorganic salts, and small amounts of organic matter present in solution of water. The principal constituents are usually calcium, magnesium, sodium, and potassium cations and carbonate, chloride, sulphate and nitrate anions. TDS in water supplies originate from natural sources, sewage, urban and agricultural run-off, and industrial waste water. (WHO, 2004). The palatability of water with a TDS level of about 600 mg/L is generally considered to be good and drinking water becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 mg/L (WHO, 2011).

Total dissolved solids and conductivity both indicate the total inorganic mineral content of drinking water. Either of these tests can be used to monitor the consistency of quality from water purification processes, which remove inorganic contaminants from water.

2.5 Conventional Water Treatment Process

Conventional water treatment is defined as the sequential use of coagulation, flocculation, sedimentation, filtration, and disinfection (normally with chlorine) in drinking water treatment (EPA, 2002). Coagulation is employed to remove colloidal matter, suspended solids with negligible settling velocity (Tchobanoglous, 2003). Because most naturally occurring colloids are negatively charged, they are maintained in suspension by the repulsive force of their like charges (Letterman *et al.*, 1999). Conventional treatment is

often preceded by pre-sedimentation, may be accompanied by addition of powdered activated carbon (PAC) addition, utilize granular activated carbon (GAC) as a filter media, and then be followed by GAC adsorption. Conventional treatment is often preceded by pre-oxidation, or oxidation taking place concurrently. Oxidants common to conventional treatment are chlorine, chloramine, chlorine dioxide or permanganate. Occasionally membrane processes, either membrane filtration or ultrafiltration, accompany conventional treatment. Activated carbon is commonly used to adsorb natural organic compounds, trihalomethanes (THMs) taste and odor compounds, and other synthetic organic chemicals in drinking water treatment. (EPA, 2002).

2.5.1 Coagulation and flocculation

In conventional turbidity removal processes, Pernitsky and Edzwald (2006) state that coagulation using metal based coagulants (Al, Fe) was considered as a destabilization process of colloidal particles, involving two primary coagulation mechanisms: which are charge neutralization of the negatively charged colloidal particles by adsorption of positively charged coagulant species, followed by enmeshment of the colloids in precipitated metal hydroxide solids, i.e. $\text{Al}(\text{OH})_3$, $\text{Fe}(\text{OH})_3$ (Amirtharajah & Mills, 1982).

When a coagulant, e.g. hydrolyzing metallic salt, is added to water, it dissociates; the metallic ions undergo hydrolysis, creating positively-charged complexes (Reynolds and Richards, 1996; Letterman *et al.*, 1999). These complexes adsorb to the surface of colloidal particles, thereby reducing their electrostatic forces. This reduction in repulsive, electrostatic forces destabilizes the colloidal particles hence they aggregate during the subsequent flocculation process, causing them to settle or be filterable as flocs (Smethurst, 1988). This type of coagulation is referred to as charge neutralization (Letterman *et al.*, 1999). Flocculation is the agglomeration of destabilized particles into micro-flocs and then into bulky floccules which sediment leaving the water clearer. While the coagulation process destabilizes particles through chemical reactions between the coagulant and the suspended colloids, flocculation is the transport step that causes the necessary collisions between the destabilized particles and subsequent floc aggregations (Smethurst, 1988).

The small particles are stabilized (kept in suspension) by the action of physical forces on the particles themselves (Letterman *et al.*, 1999). One of the forces playing a dominant role in stabilization results from the surface charge present on the particles. Most solids suspended in water possess a negative charge and, since they have the same type of surface charge, repel each other when they come close together. Therefore, they remain in suspension rather than clump together and settle out of the water. An increasing positive signal may be an indication of charge reversal and particle destabilization. Once particle destabilization is achieved, this set point is maintained by adjusting the coagulant dose either manually or automatically. During flocculation, the particles are drawn together by van der Waal's forces, forming floc. The coagulation - flocculation process is affected by pH, turbidity, temperature, mixing, and coagulant chemicals (AWWA, 2000).

The efficiency of the coagulation process depends on the raw water properties, the coagulant used and operational factors including mixing conditions, coagulant dose rate and pH value. The choice of coagulant and determination of optimum operating conditions for a specific raw water source have to be determined by bench-scale coagulation tests ('jar tests').

Proper coagulation is essential for good clarification and filtration performance and for the control of pathogens and disinfection by-products. Improper coagulation can cause high coagulant residuals in treated water and post-treatment precipitation of particles causing turbidity, deposition and coatings of pipes in the distribution system. (Pernitsky & Edzwald, 2006). The single most important factor influencing the effectiveness of water treatment, particularly coagulation, flocculation and clarification is probably the consistency of the raw water supply (EPA, 2002).

2.5.1.1 Factors Influencing Coagulation

In a well-run conventional water treatment plant, adjustments are often necessary in order to maximize the coagulation - flocculation process. These adjustments are a reaction to changes in quality of the raw water entering the plant. Coagulation will be affected by changes in the water's pH, alkalinity, temperature, time, velocity and zeta potential.

Alkalinity is needed to provide anions, such as (OH) for forming insoluble compounds to precipitate them out. It could be naturally present in the water or needed to be added as hydroxides, carbonates, or bicarbonates. Generally 1 part alum uses 0.5 parts alkalinity for proper coagulation. The higher the temperature, the faster the reaction, and the more effective is the coagulation. Zeta potential is the charge at the boundary of the colloidal turbidity particle and the surrounding water. The higher the charge the more is the repulsion between the turbidity particles, the less the coagulation, and vice versa. Higher zeta potential requires the higher coagulant dose. An effective coagulation is aimed at reducing zeta potential charge to almost zero. In many instances, coagulant demand tests are made about three times a week or more frequently if significant raw water quality changes are expected such as following heavy rains (AWWA, 2000).

2.5.1.2 Turbidity

Turbidity is a principal physical characteristic of water and is an expression of the optical property that causes light to be scattered and absorbed by particles and molecules rather than transmitted in straight lines through a water sample (EPA, 1999). It is caused by suspended matter or impurities that interfere with the clarity of the water. These impurities may include clay, silt, finely divided inorganic and organic matter, soluble colored organic compounds, and plankton and other microscopic organisms.

Nephelometry has been adopted by Standard Methods as the preferred means for measuring turbidity because of the method's sensitivity, precision, and applicability over a wide range of particle size and concentration. The preferred expression of turbidity is NTU (EPA, 1999). Turbidity measurement gives a quantitative indication of the clarity of water and analysis is carried out using a nephelometer, which measures the intensity of light scattered in one particular direction, usually perpendicular to the incident light and are relatively unaffected by dissolved colour. Nephelometers are calibrated against turbidity standards prepared from a suspension of formazin and the standard unit of turbidity is the nephelometric turbidity unit or NTU (EPA, 1999).

The characteristics of turbidity in surface water supplies are a function of many factors. Watershed features, such as geology, human development (i.e., agricultural uses or urban development), topography, vegetation, and precipitation greatly influence raw water turbidity (EPA, 1999). The largest component comprising the mix of particles creating turbidity found in rivers is caused by erosion of materials from the contributing watershed. Turbidity may be created from a wide variety of eroded materials, including clay, silt, or mineral particles from soils, or from natural organic matter created by the decay of vegetation. Particles may capture and hide, or mask, other inorganic and organic constituents that are present in the watershed (EPA, 1999). Turbidity is also an important operational parameter in process control and can indicate problems with treatment processes, particularly coagulation/sedimentation and filtration. Particulates can protect microorganisms from the effects of disinfection and can stimulate bacterial growth, therefore turbidity must be low so that disinfection can be effective. (WHO, 2008).

Total organic carbon (TOC) is an aggregate parameter of different fraction of Natural Organic Matter (NOM). Since, the United States Environmental Protection Agency has proposed the TOC parameter as a measure of DBP precursors (EPA, 1989), several researchers have investigated NOM in more details by the isolation and fractionation the NOM into minor fractions. Generally, water sample with higher content of NOM will form higher level of THM during the chlorination process. (Leenherr, 1981). The Kenya Standards for Drinking Water (KS 459-1:2007) includes turbidity as an indicator parameter with a numeric standard requirement for treated surface waters with the values between 0 - 5 NTU.

2.5.1.3 pH and alkalinity

The pH value of water is a measure of acidity or alkalinity. Routine monitoring of raw water should provide baseline information about normal pH and alkalinity values. Water is neutral when the numbers of hydrogen ions and hydroxide ions are equal (AWWA, 2000). When the concentration of hydrogen ions exceeds that of hydroxide ions, the water is acidic and has a pH value less than 7. Conversely, when the concentration of hydroxide

ions exceeds that of hydrogen ions, the water is alkaline and has a pH value greater than 7. Alkalinity is the acid absorbing property of water.

The pH scale is logarithmic, therefore a change in pH value of one unit represents a tenfold change in the concentrations of hydrogen and hydroxide ions meaning that for each 1.0 unit change of pH, acidity or alkalinity changes by a factor of 10.0; that is, a pH of 5.0 is ten times more acidic than 6.0. Acidity in raw water can result from the dissolution of carbon dioxide to produce weak carbonic acid. Surface waters may also contain organic acids produced during the decomposition of vegetation. (EPA, 2006).

For a specific coagulant (such as aluminium sulphate), the pH determines which hydrolysis species (chemical compounds) predominate. Lower pH values tend to favour positively charged species, which are desirable for reacting with negatively charged colloids and particulates, forming insoluble flocs and removing impurities from the water.

The optimum pH for alum coagulation, which is very dependent on the water being treated, usually falls in the range of pH 5 to 8, approximately. The aluminium hydroxide floc is insoluble over a relatively narrow bands of pH, which may vary with the source of the raw water. Therefore pH control is important in coagulation, not only in the removal of turbidity and colour but also to achieve the minimum level of dissolved residual aluminium in the clarified water. Residual alkalinity in the water serves to buffer the system (prevent pH from changing) and aids in the complete precipitation of the coagulant chemicals. The amount of alkalinity in the source (raw) water is generally not a problem unless the alkalinity is very low. Alkalinity may be increased by the addition of lime, caustic soda or soda ash (EPA, 2002).

Alkaline waters result almost entirely from the dissolution of the bicarbonate, carbonate and hydroxide salts of calcium, magnesium, sodium and potassium. Soft acidic waters can cause corrosion of pipework and the dissolution of metals such as copper, zinc and lead. Hard, alkaline waters can cause problems associated with scale formation. The WHO guidelines for drinking water specify a numeric minimum pH value of 6.5 and a maximum

pH of 8.5. Testing water samples for total alkalinity measures the capacity of the water to neutralize acids (WHO, 2011)

A dose of 1 mg/L of aluminium sulphate reacts with 5.3 mg/L of alkalinity expressed as CaCO_3 . Thus if no alkali is added the alkalinity will be reduced by this amount with a consequent reduction in pH. The aluminium hydroxide floc is insoluble over relatively narrow bands of pH, which may vary with the source of the raw water. Therefore pH control is important in coagulation, not only in the removal of turbidity and colour but also to maintain satisfactory minimum levels of dissolved residual aluminium in the clarified water. The optimum pH for the coagulation of lowland surface waters is usually within the range 6.5 to 7.5, whereas for more highly coloured upland waters a lower pH range, typically 5.5 to 6.5 is necessary (EPA, 2002).

2.5.1.4 Temperature

Low temperatures affect coagulation - flocculation processes by altering coagulant solubility, increasing water viscosity, retards the kinetics of hydrolysis reactions and particle flocculation (Pernitsky *et al.*, 2006). Temperature affects the density of water, and as temperature decreases through its normal surface temperatures from 25°C to 4°C, water increases in density. From Stokes' Law, as the difference between the density of the particle and the density of water increases, the settling velocity of the particle increases. From Stokes' Law, the velocity at which a particle settles is inversely proportional to the viscosity. Viscosity of water increases as the temperature decreases thus, as water decreases in temperature, the twin effects of increased density and increased viscosity reduce the settling velocity of particles. Most of the suspended solids of concern in water treatment settle in accordance with Stokes' law where the dynamic viscosity of water varies inversely with temperature so that water at 0°C has twice the dynamic viscosity of water at 25°C. The theory applies to discrete particles, while in the settling tank of a treatment works, the norm would be hindered settling (EPA, 2002).

2.6 Nitrates and Phosphates

Agricultural pollution is both a direct and indirect cause of human health impacts. The WHO reports that nitrogen levels in groundwater have grown in many parts of the world as a result of "intensification of farming practice" (WHO, 1993). This phenomenon is well known in parts of Europe. Nitrate levels have grown in some countries to the point where more than 10% of the population is exposed to nitrate levels in drinking water that are above the 10 mg/L guideline. Although WHO finds no significant links between nitrate and nitrite and human cancers, the drinking water guideline is established to prevent methaemoglobinaemia to which infants are particularly susceptible (WHO, 1993).

The United States Environmental Protection Agency (USEPA) 1986 report to Congress indicated that 65% of assessed river miles in the United States were impacted by non-point sources and in its later study in 1994, identified agriculture as the leading cause of water quality impairment of rivers and lakes in the United States with sediments, nutrients and pesticide as the significant pollutants associated with agriculture (FAO, 1993). In the developing countries, it is usually wells in villages or close to towns that contain the highest levels, suggesting that domestic excreta are the main source, though livestock wastes are particularly important in semi-arid areas where drinking troughs are close to wells (Avcievala, 1991).

Although both nitrogen and phosphorus contribute to eutrophication, classification of trophic status usually focuses on that nutrient which is limiting. In the majority of cases, phosphorus is the limiting nutrient. While the effects of eutrophication such as algal blooms are readily visible, the process of eutrophication is complex and its measurement difficult. The precise role of agriculture in eutrophication of surface water and contamination of groundwater is difficult to quantify. Where it is warranted, the use of environmental isotopes can aid in the diagnosis of pollutant pathways to and within groundwater. Isermann (1990) calculated that European agriculture is responsible for 60% of the total riverine flux of nitrogen to the North Sea, and 25% of the total phosphorus loading (Ongley, 1996). Environmental nitrate and nitrite formation occurs both naturally

and through anthropogenic processes. Naturally, nitrate and nitrite are products of the oxidation of nitrogen by microorganisms in plants, soil and water and, to a lesser extent, by lightning (WHO, 2008).

Anthropogenic processes are the most common sources of both nitrate and nitrite. These sources include agricultural activities (including inorganic ammonium nitrate fertilizers and organic nitrates livestock manures and animal feedlots), wastewater treatment, nitrogenous waste products in human and other animal excreta, and discharges from industrial processes. Nitrate and nitrite can be produced as a result of nitrification process in source water or distribution systems, which add ammonia as part of chloramine disinfection practices (WHO, 2008).

2.6.1 Phosphorus Removal Processes

Membrane technologies have been of growing interest for wastewater treatment in general, and most recently, for phosphorus removal in particular. In addition to removing the phosphorus in the TSS, membranes also can remove dissolved phosphorus. Membrane bioreactors (MBRs, which incorporate membrane technology in a suspended growth secondary treatment process), tertiary membrane filtration (after secondary treatment), and reverse osmosis (RO) systems have all been used in full-scale plants with good results (Strom, 2006).

Chemical precipitation has also long been used for phosphorus removal. The chemicals most often employed are compounds of calcium, aluminum, and iron (Tchobanoglous *et al.*, 2003). A major concern with chemical precipitation for phosphorus removal continues to be the additional sludge that result, however use of alum after secondary treatment can be predicted to produce much less sludge (Strom, 2006). Phosphorus removal from wastewater has long been achieved through biological assimilation – incorporation of the phosphorus as an essential element in biomass, particularly through growth of photosynthetic organisms (plants, algae, and some bacteria, such as cyanobacteria). Traditionally, this was achieved through treatment ponds containing planktonic or

attached algae, rooted plants, or even floating plants (e.g., water hyacinths, duckweed) (Strom, 2006).

2.6.2 Nitrate removal from drinking water

The most commonly used nitrate treatment method is Ion Exchange (IE). Nitrate is removed from the treatment stream by displacing chloride on an anion exchange resin. Subsequently, regeneration of the resin is necessary to remove the nitrate from the resin. Regeneration is accomplished by using a highly concentrated salt solution resulting in the displacement of nitrate by chloride.

The second most common nitrate treatment alternative is Reverse Osmosis. Reverse Osmosis can be feasible for both municipal and Point-of-Use applications and can be used simultaneously for desalination and removal of nitrate and many co-contaminants. Water is forced through a semi-permeable membrane under pressure such that the water passes through, while contaminants are impeded by the membrane (Vivian, 2012). Nitrate ions can also be removed by use of Electro-Dialysis (ED) in potable water treatment. This technology offers the potential for lower residual volumes through improved water recovery, the ability to selectively remove nitrate ions, and the minimization of chemical and energy requirements. ED works by passing an electric current through a series of anion and cation exchange membranes that trap nitrate and other ions in a concentrated waste stream. To minimize fouling and thus the need for chemical addition, the polarity of the system can be reversed with electro-dialysis reversal (EDR). The World Health Organization guideline values prescribed for drinking water are; Nitrates is 10 mg/L as Nitrate – Nitrogen and Nitrites is 3mg/L as NO^{-2} (WHO, 2011).

2.6.3 Algal Growth within Water Treatment Works

Toxin-producing cyanobacteria are a growing concern for water utilities that use surface water (Ongley, 1996). Surface water quality in terms of nutrients Nitrates and Phosphorus (N and P), dissolved oxygen, silica, carbon dioxide, macro and micro nutrients, pH effects have direct impact on algal growth. Climatic factors including sunlight, temperature and

water movement also play an important role in promoting or limiting the algal growth. Water quality in treatment plant is impacted due to algal growth, and a direct impact is seen on total organic carbon (TOC) and disinfection by-products (Sunil, 2009).

With proper coagulation and flocculation, the sedimentation and filtration processes generally provide good blue-green algal cell removal. If the toxins are released into the water due oxidation by chlorination causing cell damage and/or natural decay, sedimentation and filtration would not provide sufficient removal. The goal of conventional treatment should be undisruptive transport, removal, and disposal of healthy, intact blue-green algal cells. Each process should be evaluated for cell removal performance and optimized to mitigate the risk of cell breakdown and/or release of dissolved toxins hence if pre-oxidation of the raw water is practiced, special precautions must be taken (EPA, 2011). Design considerations including covered sedimentation basins and filters, algaecide coatings on walls, application of algaecides like copper sulphate and potassium permanganate help in controlling algae to some extent. Operational practices like scrubbing walls and using strong oxidants like ozone and chlorine dioxide also aid in algae control. Some emerging techniques including enhanced coagulation, ozoflotation, dissolved air flotation (DAF), and ultrasonication appear to have potential in limiting algal growth and improving performance and water quality (Sunil, 2009). While confirmed occurrences of adverse health effects in humans are rare, some incidents have been documented worldwide (AWWA, 2010).

2.7 Legal Framework for Domestic water in Kenya

2.7.1 Environmental Management and Co-ordination Act (EMCA), 2006

Environmental Management and Coordination (Water Quality) Regulations 2006 apply to drinking water, water used for industrial purposes, water used for agricultural purposes, water used for recreational purposes, water used for fisheries and wildlife, and water used for any other purposes in Kenya. Part (II) of these regulations deals with protection of sources of water for domestic use. Regulation 9, of the rules provide that the Authority in consultation with the relevant lead agency, shall maintain water quality monitoring for

sources of domestic water at least twice every calendar year. Table 2.1 shows the numeric criteria for sources of domestic water as provided in the EMCA (Water Quality) Regulations, 2006 and adopted by the Kenya Bureau of Standards. The maximum allowable value is the contaminant level in water which is delivered to any user of a public water system.

2.7.2 Public Health Act

The Kenya Public Health Act Chapter 242, Part XI stipulates that it is the duty of local authority to ensure protection of water supplies and therefore take all lawful, necessary and reasonably practicable measures for preventing any pollution dangerous to health, of any supply of water which the public within its district has a right to use and does use for drinking or domestic purposes (GoK, 2012).

2.7.3 Water Act

The Kenya Water Act 2016, Part II (10) mandates the Water Resources Authority with formulation of National Water Resource Strategy to provide for the management of water resources. The Strategy should contain, among other things, details of; existing water resources and their defined riparian areas, measures for the protection, conservation, control, management of water resources and approved land use for the riparian area, minimum water reserve levels at national and county levels (GoK, 2016). WRMA Water Rules and Regulations 2007 (Part IX – 116) defines riparian land of a river as the land 6 metres on each side of a water course or equal to full width of watercourse up to a maximum of 30 m on either side of bank. Riparian land does not imply change of ownership but only imposes management controls on land use for water resource quality.

Table 2.1: Quality standard for sources of domestic water

	Parameter	Guide value (Maximum Allowable)
1.	pH	6.5 – 8.5
2.	Suspended Solids	30 (mg/L)
3.	Nitrate –NO ₃	10 (mg/L)
4.	Ammonia – NH ₃	10 (mg/L)
5.	Nitrite – NO ₂	3 (mg/L)
6.	Total Dissolved Solids	1200 (mg/L)
7.	<i>E. coli</i>	Nil/100ml
8.	Fluoride	1.5 (mg/L)
9.	Phenols	Nil (mg/L)
10.	Arsenic	0.01 (mg/L)
11.	Cadmium	0.01 ((mg/L)
12.	Lead	0.05 (mg/L)
13.	Selenium	0.01 (mg/L)
14.	Copper	0.05 (mg/L)
15.	Zinc	1.5 (mg/L)
16.	Alkyl benzyl sulphonates	0.5 (mg/L)
17.	Permanganate value (PV)	1.0 (mg/L)

The guide values in Table 2.1 are as defined in the Environmental Management and Coordination (Water Quality) Regulations 2006.

2.8 Previous works relevant to the study

A Water Quality Assessment study of the Owena Multi-Purpose Dam in Nigeria was conducted in which water samples were taken from the dam in six sampling campaigns covering the wet and dry seasons and analyzed for physico-chemical and microbial characteristics using standard methods for the examination of water and wastewater jointly published by the American Public Health Association, American Water Works Association and Water Pollution Control Federation. Results showed significant ($p < 0.05$) seasonal variations in most measured parameters with few showing significant spatial variation. The characteristics of the water from the lake revealed an acceptable quality for most measured parameters with low chemical pollutants burden when compared with drinking water standards and water quality for aquaculture. However, high values of turbidity, colour, iron, manganese and microbial load were recorded compared with drinking water standards which therefore required proper treatment of the water before distribution for public consumption (Oyhakilome, 2011).

Napacho and Manyele (2010) conducted a study on drinking water quality in Temeke District (Dar es Salaam), which involved analyses of chemical parameters of drinking water samples from different drinking water sources. The drinking water sources examined included tap water, river water and well water (deep and shallow wells). Water quality parameters studied included pH, chloride, nitrate and total hardness levels. The concentrations of total hardness in mg CaCO₃/L and chloride were obtained by titration method while the nitrate concentration levels were determined by spectrophotometry. The study revealed that the chemical parameters of water sources did not meet the permissible World Health Organization (WHO) and Tanzania Bureau of Standards (TBS) levels. Examining exceedance above the WHO standards, it was revealed that most of the samples contained chloride levels above allowable WHO limits. It was recommended that drinking water sources for domestic use should be protected from pollution sources.

A Study conducted at Masinga Dam in Kenya, whose main catchment basin is the Upper - Tana showed that highest sediment loading into the rivers and ultimately into Masinga Dam is more pronounced during rainy season and increases with rain intensity and duration. Sediment loading is highest during the long rain season (March - May) as compared to the short rain season (October – December). Since water is the medium of sediment loading, there is a strong correlation between catchment precipitation trends and sediment loading into the dam. For instance sediment loading in River Thika has the highest rate of 87.38 m³/s in the month of May during the long rain season of 2010 and least in October just before the onset of short rains in the same year at 0.85m³/s (Martin *et al*, 2013).

According to a baseline review report on the Upper Tana catchment by Geertsema (2009), Lower Chania sub-catchment is drained by Chania River which enters the catchment at Ragia location in Nyandarua South District flowing downstream to the confluence of Thika and Chania rivers behind Blue Post Hotel. It covers an approximate distance of 50 Km, and area of 750 km². Besides the tributaries the sub-catchment has several streams, springs, wetlands, boreholes, and dams. Water quality in this sub-catchment has been on the decline over the years due to increase in both point and non-point sources of pollution. Within Lower Chania sub-catchment pollution occurs at different levels. The main point sources of pollution within the sub-catchment includes but not limited to effluence from agro-based industries like coffee factories and car washing (Geertsema, 2009).

2.9 Analytical Procedures

2.9.1 Spectrophotometry

Spectrophotometry is a method to measure how much a chemical substance absorbs light by measuring the intensity of light as a beam of light passes through sample solution. The basic principle is that each compound absorbs or transmits light over a certain range of wavelength (Prabhakar, 2002). This measurement can also be used to measure the amount of a known chemical substance. UV-visible spectrophotometer uses light over the

ultraviolet range (185 - 400 nm) and visible range (400 - 700 nm) of electromagnetic radiation spectrum (Prabhakar, 2002). A Spectrometer produces a desired range of wavelength of light, first a collimator (lens) transmits a straight beam of light (photons) that passes through a monochromator (prism) to split it into several component wavelengths (spectrum). Then a wavelength selector (slit) transmits only the desired wavelengths. After the desired range of wavelength of light passes through the solution of a sample in cuvette, the photometer detects the amount of photons that is absorbed and then sends a signal to a digital display (Bessell, 1999).

2.9.2 Total-Reflection X-Ray Fluorescence (TXRF) Spectroscopy

The main principle of X-Ray Fluorescence Spectroscopy (XRF) is based on the fact that atoms, when irradiated with X-Rays, radiate secondary X-Rays - the fluorescence radiation (Klockenkämper, 2015). On this basis XRF-analysis is possible because the wavelength and energy of the fluorescence radiation is specific for each element and the concentration of each element can be calculated using the intensity of the fluorescence radiation (Klockenkämper, 2015).

2.9.3 Flame Atomic Emission Spectrometry

Atomic emission is a result of electrons dropping from an excited state to lower states (Marvin, 1956). When a sample solution is sprayed into flame, the solvent evaporates and ions are converted into atomic state. In the heat of the flame, small fraction of the atoms is excited (De Oliveira, 2009). Relaxation of the excited atoms to the lower energy level is accompanied by emission of light (photons) with characteristic wavelength. Intensity of the emitted light depends on the concentration of particular atoms in flame. This emitted radiation passes through a monochromator that isolates the specific wavelength for the desired analysis. A photodetector measures the radiant power of the selected radiation, which is then amplified and sent to a readout device, meter, recorder, or microcomputer system (Xiaowei, 1991).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study design

Experimental research design was used to establish the physico-chemical and microbial quality of water and utilized primary data to address the three specific objectives of the study. Triplicate samples were randomly collected in 2015 from five sampling points during the dry season of August – September and during the wet season in the Months of October - December. Rainfall data for the preceding three years and that of the year of this study was also analysed to show the seasonal pattern while catchment activity data in form of photographs was used to illustrate key activities in the catchment. The quantitative data were analysed and the results were subjected to statistical analysis for hypothesis testing.

3.2 Study area

The study focused on Chania Sub – catchment and its rivers that supply water to Ng’ethu Water Works located in Kiambu County, about 70 kilometers from Nairobi City. This Sub – catchment is part of the larger Upper – Tana catchment basin of Aberdares water tower covering the counties of Nyandarua and partly Marang’a and Kiambu counties (Figures 3.1 & 3.2 below). The parameters tested included among others those listed under the EMCA (2006) Water Quality Regulations.

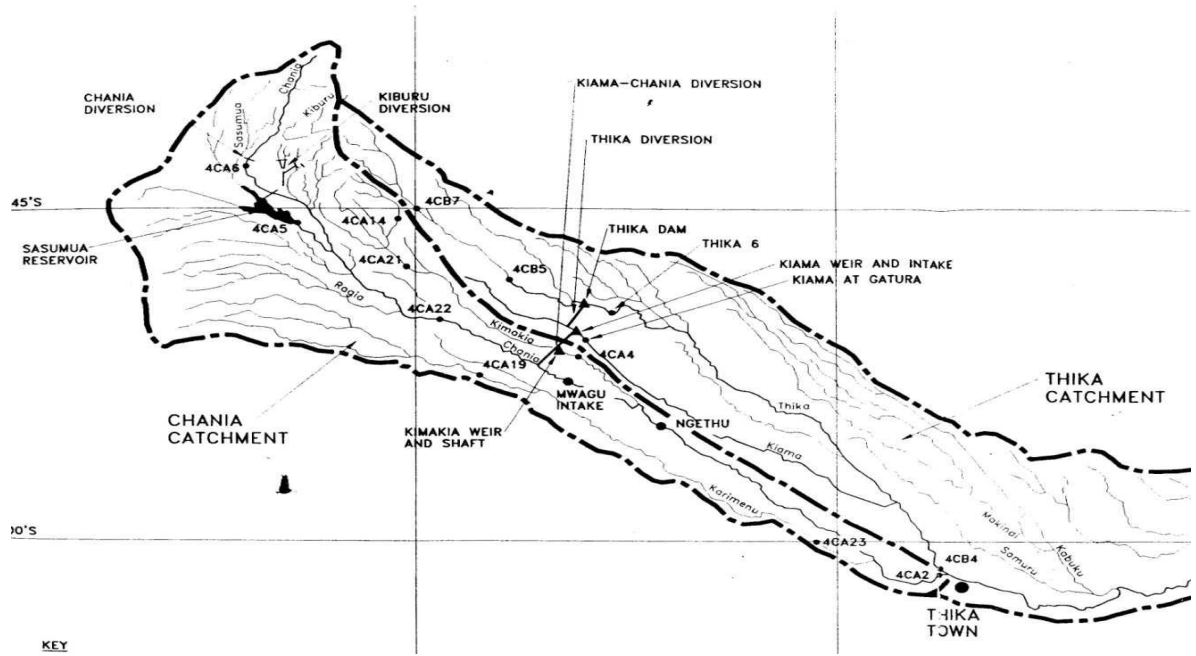


Figure 3.1: Chania Catchment Map (Hydrology Review, Howard Humphreys, 1995)



Plate 3.1: River Chania at Mataara - Sampling point

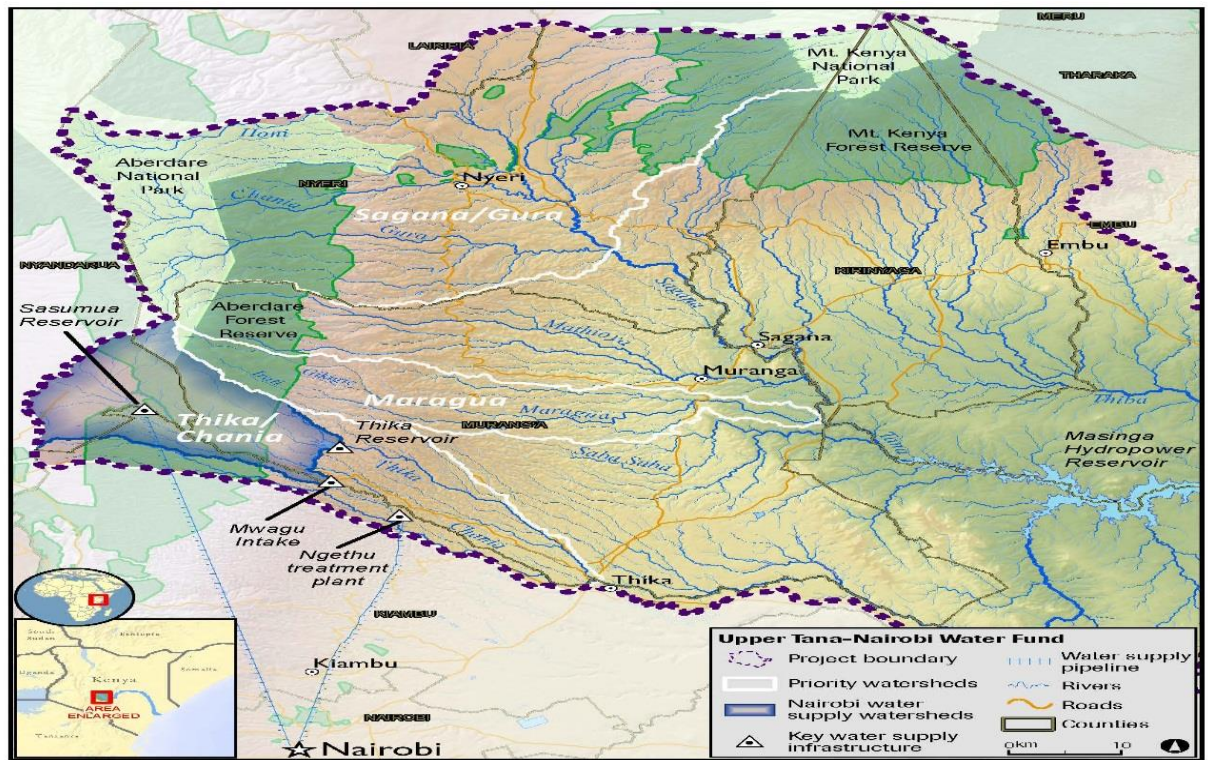


Figure 3.2: Map – Upper Tana Catchment (Water Fund Business Case - TNC, 2015)

3.3 Cleaning of research apparatus

The goal of equipment cleaning was to ensure that the apparatus were not a source of foreign substances that could affect the ambient concentrations of target analytes in samples or otherwise affect sample chemistry.

3.3.1 Cleaning of plastic ware

The samples were collected as grab samples in pre-cleaned plastic bottles in triplicates using 500 ml plastic sampling bottles which were thoroughly cleaned by washing in non-ionized detergent and rinsed with tap water and soaked in 10% HNO₃ for 24 hours and finally rinsed with de-ionized water prior to use. The bottles were rinsed three times with the water from each of the designated sampling points before sample collection. Collected

samples were promptly carried to the designated laboratory for analysis within four hours of sample collection. The equipments were pre-cleaned and no field cleaning of equipment was done. A separate set of equipment was used for each site and sampling bottles were labelled after cleaning before going to the field for sampling exercise. Abrasive cleaners, hard brushes or scouring pads which could cause scratches on surfaces were avoided.

3.3.1 Cleaning of glassware

Warm tap water with mild laboratory-grade non-ionized detergent was used and an appropriate soft brush to scrub the inside of curved glassware and de-ionized was used to wash away the tap water. The glassware were then soaked in the base bath for at least 3 hours and when putting them in the base bath, it was ensured that the glassware was completely filled with base bath and there were no air bubbles. Volumetric glassware were rinsed (both inside and outside) three times with de-ionized water after emptying and draining to prevent solutions from drying on the glassware and dried in at room temperature. Burettes tubes were thoroughly cleaned with detergent using a long brush and washings allowed to exit through the tip.

After this, the glassware were transferred to the acid bath and left to soak for 3 hours taking care to avoid air bubbles. Once this was done, they were rinsed with de-ionized water 3 times and allowed to dry on drying rack. All glassware were carefully inspected for water breaks and the cleaning process repeated if it was found necessary.

3.4 Water Sampling

Water samples were collected randomly in triplicate from five (5) strategic locations (Table 3.2) identified in the study area during the dry and wet season. During samples collection, utmost care was exercised as much as practicable to ensure a well-mixed sample was taken at least 10 cm below the water surface and well away from the river edge. In case of sampling shallow water, contamination of the sample from disturbed sediment was avoided by using an extended inlet of a thin tube on the sampling bottle. Overall, care was exercised to ensure that the analyses are representative of the actual composition of the water samples.

3.4.1 Samples for free residual chlorine

Water Samples for free residual chlorine were kept away from direct sunlight and analysis done immediately (within ten minutes) of sample collection on site.

3.4.2 Samples for TDS, Turbidity and EC analysis

Water for samples for laboratory analysis of TDS, Turbidity, EC were stored in an ice box between 1°C and 4°C in dark and analysis done within 6 hours of sample collection. The sample container was completely filled to exclude air and samples were shaken vigorously before analysis were carried out.

3.4.3 Samples for Microbiological analysis

Water samples for microbiological analysis were preserved and stored on ice between 1°C and 4°C in a sterile plastic container within 5 minutes of collection with samples holding time of 6 hours +2 hours for lab processing. For treated water (samples with residual chlorine), 0.1mL of a 10% sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution was added to dechlorinate and neutralize residual halogen within the sample water. The bottles were filled leaving approximately 2.5 cm head space.

3.4.4 Samples for analysis of Nitrate, Phosphate and Chloride

Water samples were stored between 1°C and 4°C and analyzed within 48 hours. The water samples were filtered immediately after collection and refrigerated. Filtration was done using Whatman/cellulose acetate membrane filter 0.45 µm filter paper to remove particles and turbidity before analysis. Samples for chloride analysis were stored for at room temperature and analysed within 7 days (recommended not to be stored not more than 28 days).



Plate 3.2: Treated water storage reservoir at Ng'ethu

Table 3.2: Samples collection locations

Sampling Point	ID	Coordinates-UTM ARC 1960 Zone 37S (Northing – Easting)
Chania river (Mataara bridge)	A	9906122 – 255153
Thika river (main feeder river into Thika Dam)	B	9911184 – 256230
Thika reservoir discharge(Kiama tunnel outlet)	C	9908349 – 258909
Inflow to Ng'ethu water treatment plant	D	9898032 – 266406
Treated water from plant (clear well)	E	9897855 – 266642



Plate 3.3: Thika River at weir location (Sampling point B)

3.5 Analysis Procedures

The research involved laboratory and field analysis of water samples for microbiological and physico-chemical parameters during the wet months of October - December and dry months of January – February to study the seasonal variations of different parameters as described in - Standard methods for the American Public Health Association (APHA), American Water Works Association (AWWA) and Water Pollution examination of water and waste water 21st edition prepared and published jointly by American Public Control Federation (WPCF) 2005. The measuring equipment were calibrated before use according to the manufacturer's instructions.

3.5.1 Physical Parameters

3.5.1.1 pH

pH was analyzed within three hours of sampling using digital pH meter HANNA HI 2211 using procedure described in the Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

3.5.1.2 Electrical Conductivity

Electrical Conductivity was analyzed at the sampling point using a portable EC meter (Lovibond SensoDirect Con200) using procedure described in the Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

3.5.1.3 Total Dissolved Solids

TDS was analyzed using portable TDS meter (TDS Meter 3-Hm Digital) using procedure described in the Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

3.5.1.4 Turbidity

Turbidity was analyzed in the Laboratory using a Bench Top Turbidimeter (HACH 2100N) using procedure described in the Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

3.5.2 Heavy metals analysis

The water samples were analysed for heavy metals using Total-Reflection X-Ray Fluorescence (TXRF) Spectroscopy using S2 PICOFOX Spectrometer with Gallium as internal standard for elemental quantification at University of Nairobi, Department of Nuclear Science Laboratory according to procedure described in appendix 7.

3.5.2.1 Analysis for aluminium

Analysis for aluminium was carried out by spectrophotometry method according to the standard methods for the examination of Water and waste water (APHA, 1999) using *HACH* DR 3900 visible spectrophotometer as described in appendix 10. The test results measured at 522 nm.

3.5.3 Analysis of ions

Nitrates, Phosphates and Chloride ions were analysed by spectrophotometry method as described below.

3.5.3.1 Nitrates

Nitrates ions were analysed by spectrophotometry method according to the standard methods for the examination of Water and waste water (APHA, 1999) using UV-1800 UV-VIS Spectrophotometer (SHIMADZU) with 1 cm matched quartz cells as described in appendix 12. Measurements were taken at two wavelengths, 210 nm (absorbance due to nitrates) and 275 nm (interference due to dissolved organic matter) and distilled water was used as a reference.



Plate 3.4: UV - 1800 UV-VIS Spectrophotometer (Shimadzu) (JKUAT GoK Laboratory).

3.5.3.2 Phosphate

Phosphates ions were analysed by spectrophotometry method according to the standard methods for the examination of Water and waste water (APHA, 1999) using UV-1800 UV-VIS Spectrophotometer (SHIMADZU) with 1 cm matched quartz cells as described in appendix 8. The phosphate analysed is the orthophosphate species (PO_4^{3-}) and total reactive phosphate in the samples was determined in triplicate per as indicated in appendix 8. This involved conversion of phosphate to molybdenum blue whose colour was monitored spectrophotometrically at 660nm.

3.5.3.3 Chloride

Chloride was analyzed by spectrophotometry method using *HACH* DR 3900 visible spectrophotometer according to procedure described in appendix 9 (Mercuric Thiocyanate Method 8113 - *HACH* Manual). The method is based on the formation of the characteristic iron (III) thiocyanate colour, when chloride ion reacts with mercury (II) thiocyanate in the presence of iron (III) ions. Thiocyanate ions react with the ferric ions to form an orange ferric thiocyanate complex. The amount of this complex is proportional to the chloride concentration. The measurement wavelength was 455 nm.

3.5.3.4 Sodium

Sodium was analysed by Flame Atomic Emission Spectrometry method as indicated in appendix 11 using (FAES Model AA-6200 Shimadzu) Spectrophotometer. The sodium ions were determined at low temperatures at absorbance obtained at 589 nm.

3.5.3.5 Free Residual Chlorine

Free Residual Chlorine was determined according to "Standard Methods for the Examination of Water and Wastewater, (APHA, 2005)" as an acceptable method for chlorine residual testing. DPD Colorimetric method testing was carried out using Color Disc Test Kit (Lovibond® Comparator 2000⁺). In order to carry out the test, 10 mL of water sample was taken in a tube and placed in the left compartment of the comparator. A reagent DPD (Diethyl-p-Phenylene-Diamine) chlorine tablet was placed in another tube to which 1 cm depth of water was added and the tablet allowed to dissolve. More water was now added in the tube to make 10 ml. The comparator disc was rotated till the colour matched. The residual chlorine amount was read directly from the window in the lower right corner of the instrument.

3.5.4 Microbial Analysis.

Most Probable Number (MPN) technique for detection of coliforms was used. This was done according to the standard methods for the examination of Water and waste water (APHA, 2005). The coliform bacteria was determined in three stages which are presumptive test, confirmed test and completed test.

3.5.4.1 Presumptive Test

A series of five tubes of lactose broth in three groups were inoculated with 10mls, 1ml and 0.1mls of the water. After incubation for 24 hours under 37°C, there was lactose fermentation hence production of gas and the medium changed colour from Purple to yellow. This was a presumptive evidence of presence of coliforms. The Most Probable Number (MPN) of coliforms present in the water was determined by the number of positive tubes in reference to Mc Grady's table of computation of MPN counts per 100 ml of the water sample.

3.5.4.2 The Confirmed Test

This was done by sub-culturing of the bacteria from the positive test. The bacteria was tested for the ability to grow and form colonies and produce gas in the same way on Levine's eosin methylene blue agar at 44°C for 24 hours. The production of gas indicated the positive confirmed test.

3.5.4.3 Completed Test

This was the final check for colonies which appeared on the confirmatory media. It was done by inoculating a nutrient agar slant and a tube of lactose broth. After inoculation for 24 hours at 35°C, the lactose broth was examined for gas production. A gram stained slide was made from the slant and the slide examined under oil. The organisms proved to be gram positive and this confirmed the presence of coliforms.

3.6 Data processing and analysis

In this study, data collected from the analytical methods were statistically analyzed using standard statistical methods. The values obtained from a set of observations were expressed as means and the standard deviation calculated. This was then subjected to statistical tests of significance where paired t-test was used to establish whether there existed any significant difference between concentration levels of various physico-chemical water quality parameters and heavy metal pollutants during the dry and wet seasons at the different sampling locations. All tests were conducted at 95% confidence level ($P < 0.05$).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 OVERVIEW

This chapter contains results obtained from the experimental data presented in form of tables and graphs. The mean values of the various parameters were computed, inferential statistical data analysis conducted and discussions are offered where applicable.

4.1 Physico – Chemical Parameters.

4.1.1 Turbidity (NTU)

Turbidity level in the Catchment Rivers ranged from 2.84 – 7.70 NTU during the dry season and 33.00 to 181.00NTU during the wet season. The highest mean concentration was 107.89 ± 5.85 NTU recorded during the wet season at Chania River sampling point. The turbidity levels at the storage facility in both wet and dry season were below maximum allowable levels with the highest level recorded being 1.30 ± 0.42 NTU.

The t-test results at 95% confidence level, indicated that there was a significant difference in levels of turbidity between the wet and dry season for the two rivers, Chania river and Thika river where; ($t_{cal} = 51.62$, $t_{tab} = 2.120$, $d.f = 16$, $P = 0.05$ and $t_{cal} = 20.713$, $t_{tab} = 2.120$, $d.f = 16$, $P = 0.05$) respectively. The t-test results also indicated that there was a significant difference in levels of turbidity from Thika reservoir discharge during the wet and dry season where; ($t_{cal} = 61.526$, $t_{tab} = 2.120$, $d.f = 16$, $P = 0.05$). This difference can be attributed to soil erosion from run-off mainly arising from farmlands with other dissolved substances during the wet season because of heavy rains.

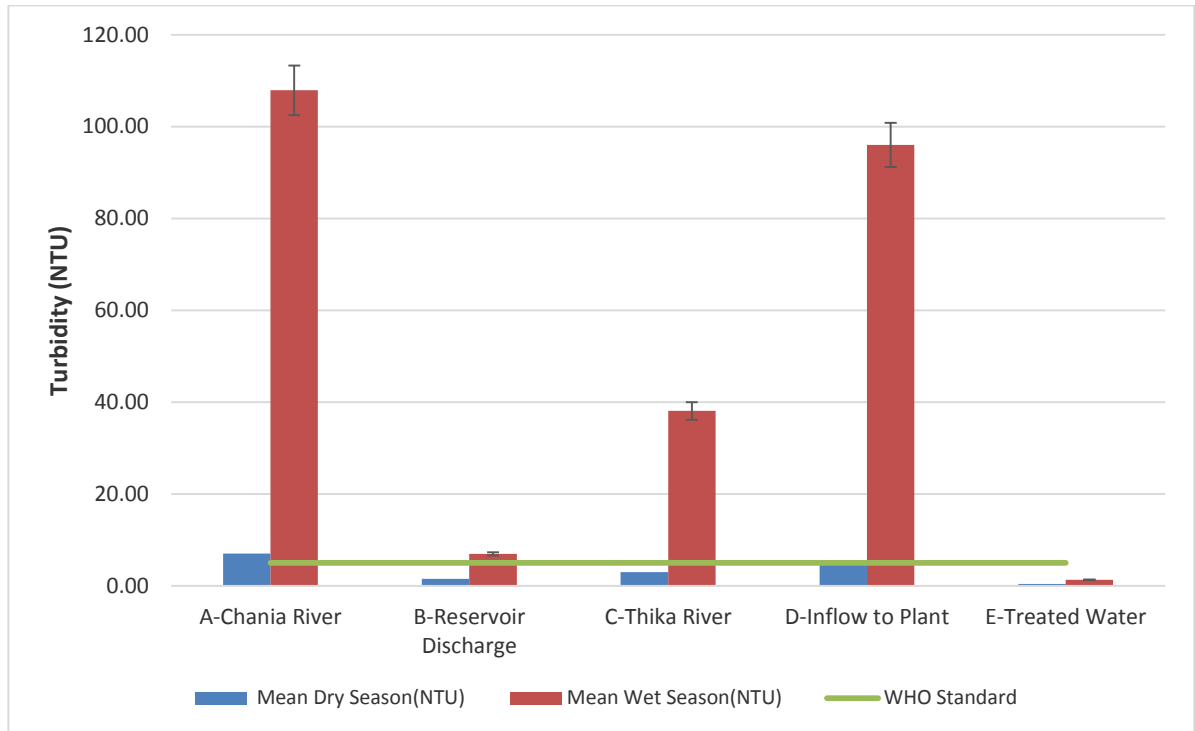


Figure 4.3: Graphical comparison of turbidity (dry & wet seasons)

The results of this study showed that the turbidity levels were above the recommended levels, according to NEMA Standards in the catchment during the wet season. However, during the dry season only Chania River recorded slightly higher levels above recommended standard of 5.0 NTU. The turbidity level was high during the wet season. This is attributed to run – off from rainfall that erodes soils from farms, dirt roads and building from stone quarry sites. Also plant remains, animal waste, fertilizers among other organic and inorganic pollutants are washed into the rivers.



Plate 4.5: Riparian Farming upstream of Chania River with tea on higher grounds

Comparing the levels of turbidity between Thika river which is the main feeder river for Thika reservoir and the discharge from the Thika reservoir, the t-test results indicated a significant difference during both the dry and wet season where; ($t_{cal} = 3.909$, $t_{tab} = 2.120$, $d.f = 16$, $P = 0.05$ and $t_{cal} = 18.38$, $t_{tab} = 2.120$, $d.f = 16$, $P = 0.05$) respectively. The significant difference in the levels of turbidity between the water in Thika river and the reservoir can be attributed to the ability stored volume of water in Thika reservoir about 50 million cubic (70% of storage capacity) to dilute the high turbidity of recharging river (Thika river).

The high turbidity level in Chania catchment during the wet season was found to be far above the acceptable limits for water meant for domestic use. The high levels of turbidity imply that there is dissolved and suspended particles in water arising from soil erosion from farmlands in the upstream slopes such as in Plate 4.5. The environment of high turbidity provides favourable climate for survival of micro-organisms and explains somewhat the reason for high MPN of coliforms during the wet season.

The mean levels of turbidity within the catchment and the treated water from the water treatment plant clear well during the wet and dry seasons are presented in Figure 4.3 and mean concentration levels are presented in Appendix 1.

4.1.2 TDS

The mean TDS values were as represented in Figure 4.4 and Appendix 1 and indicate concentration levels within the WHO recommended standards for drinking water (1000 mg/L) during both the dry and wet seasons. The mean TDS level in the catchment was found to be 24.6 mg/L.

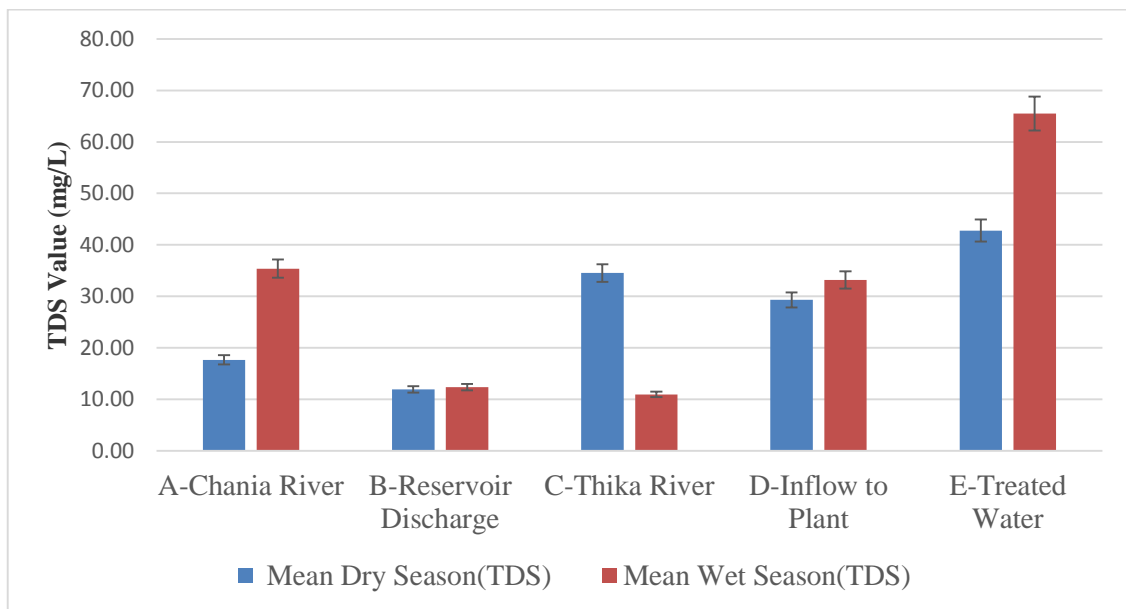


Figure 4.4: Total Dissolved Solids during the dry and wet seasons

The highest mean concentration level of TDS was 65.50 ± 2.40 mg/L recorded at Ng’ethu water treatment plant clear well during the wet season and the lowest mean level was 10.90 ± 0.37 mg/L recorded at Thika river sampling point during the wet season. The TDS levels ranged from 64.00 – 71.00 mg/L in the in the treated water clear well during the wet season and 38.06 – 55.00 mg/L during the dry season. In Thika storage reservoir, the levels were fairly constant and ranged from 11.80 – 12.70 mg/L during the wet season and 11.26 – 13.00 mg/L during the dry season. The levels in the main recharge river Thika

ranged from 10.70 – 11.80 mg/L during the wet season and 32.00 -36.04mg/L during the dry season.

The t-test results at 95% confidence level indicated that there was a significant difference between the levels of TDS in the catchment during the dry and wet seasons for Chania River and Thika River where; ($t_{cal}=47.45$, $t_{tab}=2.120$, $d.f =16$, $P=0.05$ and $t_{cal} =58.66$, $t_{tab}=2.120$, $d.f =16$, $P=0.05$) respectively. However, the t-test result for the reservoir discharge TDS mean concentration indicated that there was no significant difference during the wet and dry season where; ($t_{cal} =1.858$, $t_{tab}=2.120$, $d.f =16$, $P=0.05$).

The levels of TDS were high during the wet season in the treated water due to the fact that higher dosages of coagulant (alum) and pH adjuster (usually sodium Carbonate) are used to control turbidity and adjust pH accordingly, hence higher residuals in the treated water. The significance difference between levels of TDS between the dry and wet season can be attributed to the fact that the river water dissolves a lot of eroded substances from runoff as it flows through its course. According to World Health Organization (WHO, 2011) TDS concentration levels above 1000 mg/L makes drinking water significantly unpalatable.

4.1.3 pH

The mean pH values were as presented in Figure 4.5 and in Appendix 1. The pH levels in the catchment rivers ranged from 6.60 - 7.33 during the dry season and 6.57 - 6.80 during the wet season in the catchment rivers. The highest mean pH value in the catchment was 7.10 ± 0.22 recorded at the Thika River sampling point during the dry season while the lowest level was 6.60 ± 0.03 recorded at the same sampling point during the wet season.

The mean pH level recorded from Thika reservoir discharge was 6.80 ± 0.03 during the dry season and 6.80 ± 0.02 during the wet season indicating a relatively constant pH level. The pH in the reservoir discharge flow ranged from 6.75 - 6.85 during the dry season and 6.75

- 6.79 during the wet season. The mean pH level in the clear well during the dry season was 7.30 ± 0.15 while during the wet season it was 7.30 ± 0.16 .

The *t-test* results indicated that there was a significant difference between pH level during the dry season and the wet season in Chania river and Thika river where; ($t_{cal} = 10.733$, $t_{tab} = 2.120$, $d.f = 16$, $P = 0.05$ and $t_{cal} = 6.756$, $t_{tab} = 2.120$, $d.f = 16$, $P = 0.05$) respectively. The *t-test* results from the reservoir discharge indicated that there was no significant difference in pH between the dry and wet season where; ($t_{cal} = 0.8321$, $t_{tab} = 2.120$, $d.f = 16$, $P = 0.05$).

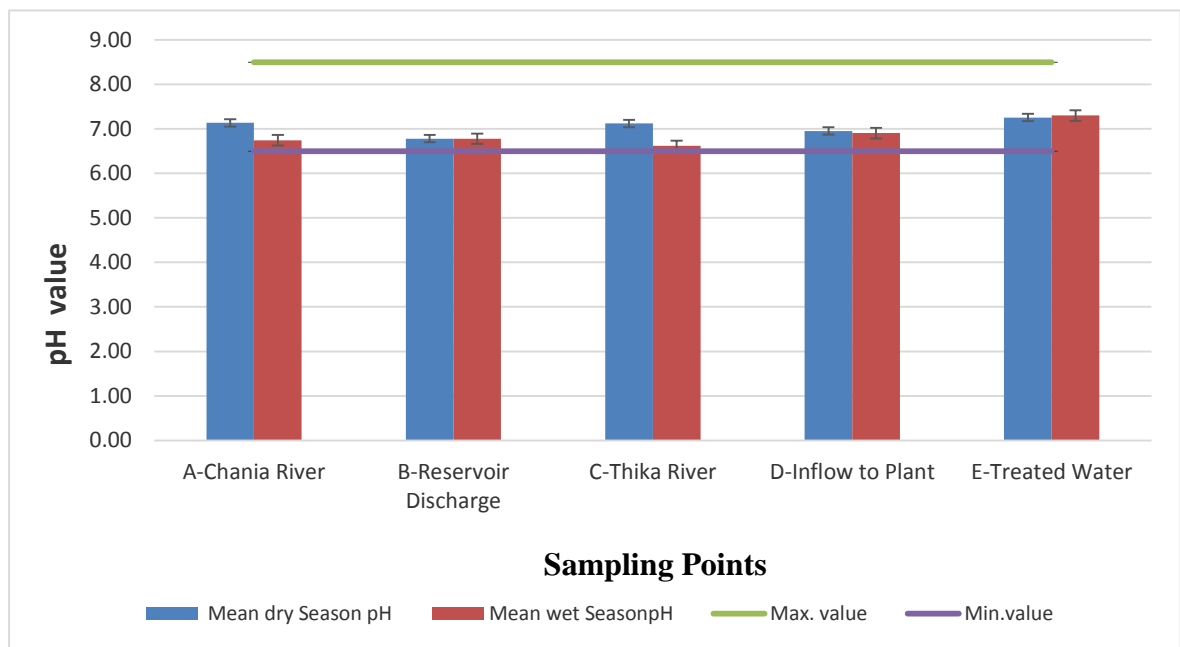


Figure 4.5: pH during the dry and wet seasons

There was however no significant difference in pH levels in the treated water from the clear well between the dry and wet season where; ($t_{cal} = 0.684$, $t_{tab} = 2.120$, $d.f = 16$, $P = 0.05$). This is attributed to the fact that the pH of treated water is usually adjusted to drinking water standards by use of sodium carbonate. The World Health Organisation guidelines for drinking water specify a numeric minimum pH value of 6.5 and a maximum pH of 8.5 (WHO, 2011).

In this study the pH was found to fall within the recommended levels during the wet and dry season with the wet season pH levels just slightly lower than in the dry season. Acidity in raw water can result from the dissolution of carbon dioxide to produce weak carbonic acid. Surface waters may also contain organic acids produced during the decomposition of vegetation (EPA, 2006). The mean pH level in the catchment was found to be 6.91 ± 0.26 implying the level is within recommended drinking water standards.

4.1.4 Electrical Conductivity ($\mu\text{S}/\text{cm}$)

The EC levels were as presented in Figure 4.6 and appendix 1. The highest mean EC level in the catchment was $52.32 \pm 1.15 \mu\text{S}/\text{cm}$ recorded at the Chania River sampling point during the wet season. The lowest mean EC concentration was $16.64 \pm 0.40 \mu\text{S}/\text{cm}$ recorded at the Thika River sampling point in the river during the wet season. The mean EC levels during the wet season were higher than those measured during the dry season except in Thika River. EC level in the catchment ranged from 26 – 58 $\mu\text{S}/\text{cm}$ during the dry season and 16 – 54 $\mu\text{S}/\text{cm}$ during the wet season.

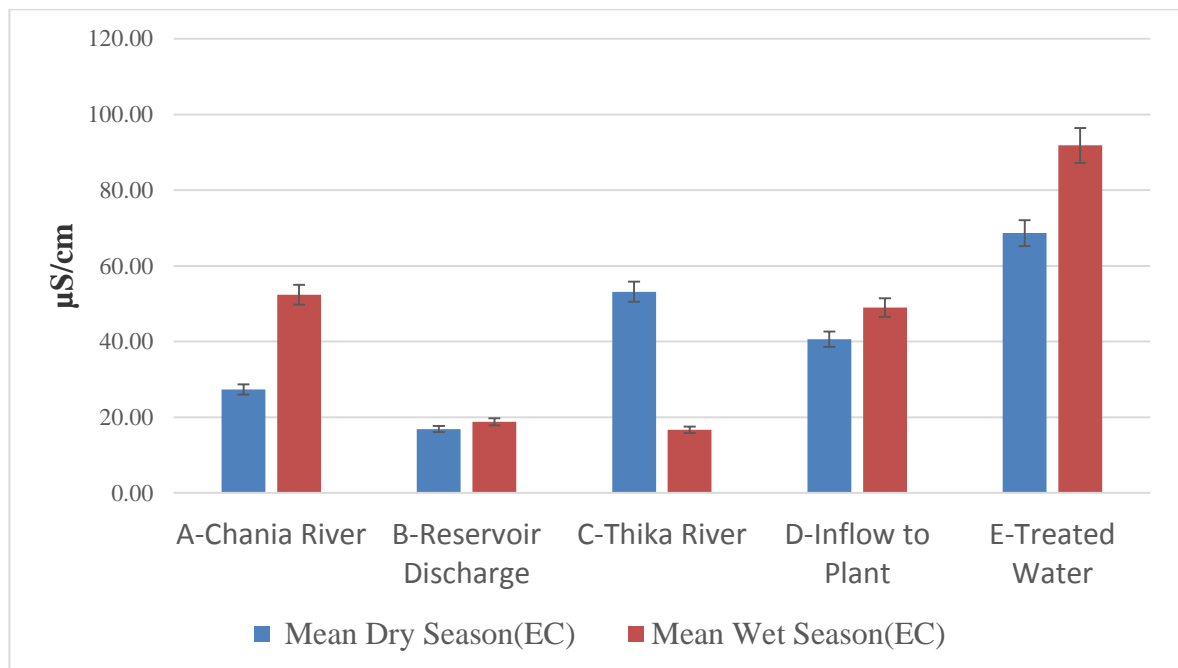


Figure 4.6: Electrical Conductive during the dry and wet seasons

Measurements from Thika reservoir discharge levels ranged from 16.6 – 17.5 $\mu\text{S}/\text{cm}$ during the dry season and 18.40 – 19.20 $\mu\text{S}/\text{cm}$ during the wet season. The EC Levels in the clear well during the dry season ranged from 61.00 – 80.0 $\mu\text{S}/\text{cm}$ while during the wet season they ranged from 86.00 - 95.00 $\mu\text{S}/\text{cm}$.

The t-test indicated that there was a significant difference between the levels of EC between the dry and wet seasons in Chania river and Chania river where; ($t_{cal}=38.094$, $t_{tab}=2.120$, $d.f=16$, $P=0.05$ and $t_{cal}=40.813$, $t_{tab}=2.120$, $d.f=16$, $P=0.05$) respectively. The t-test result for Thika reservoir discharge also indicated a significant difference in EC levels between the dry and wet season where; ($t_{cal}=14.65$, $t_{tab}=2.120$, $d.f=16$, $P=0.05$).

There was also a significant difference between EC level during the dry season and the wet season in the treated water where; ($t_{cal}=10.338$, $t_{tab}=2.120$, $d.f=16$, $P=0.05$). The levels were higher in the clear well than in the raw water this can be attributed to residual chemicals like sodium carbonate, chlorine and aluminium sulphate used to treat the water. Changes in conductivity with time, or high conductivity values, can both indicate that the water has become contaminated for example from saline intrusion, nutrients pollution etc. The mean EC level at the different sampling points is as presented in Appendix A1.

4.1.5 Temperature

This was determined on site while sampling. A standardized pocket thermometer was immersed in the water sample and the readings taken.

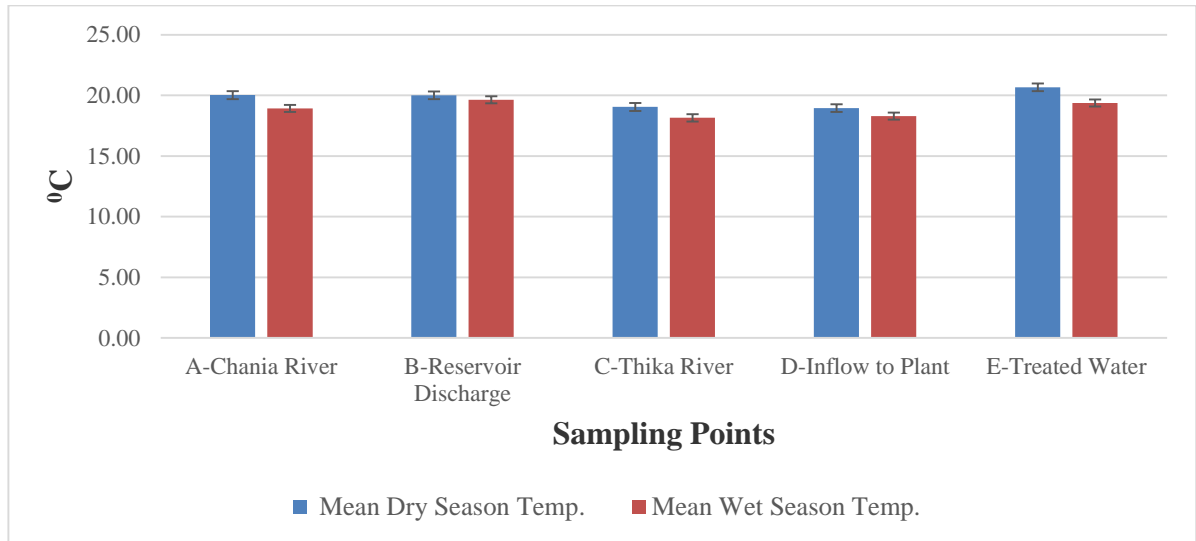


Figure 4.7: Water Temperature during the dry and wet seasons

In this study, the mean water temperature in the Catchment Rivers at the different sampling points was as presented in Appendix 1 and Figure 4.7. The water temperature was found to be slightly higher during dry season than in the wet season and fell within the range of 18.5 – 20.1 °C during the dry season and 18.0 – 20.0 °C during the wet season. The highest mean water temperature value in the catchment was 20.0±0.10 °C recorded at Chania River sampling point during the dry season while the lowest level was 18.1±0.21°C recorded at Thika river sampling point during the wet season. The mean water temperature of water entering the treatment plant was 18.9±0.30 °C during the dry season and 18.3±0.35 °C during the wet season. However, the treated water temperature was higher during both the dry and wet seasons with a range of 20.5 – 21.0 °C during the dry season and 19.0 – 20.0 °C during the wet season.

Water temperature affects the coagulation process because viscosity is directly proportionate to temperature of water, thus lower temperature waters decrease the hydrolysis and precipitation kinetics. However, most coagulants work more effectively in water temperatures above 12 °C (EPA, 2002). Therefore the range of temperatures recorded in this study is expected to enhance coagulation.

4.2 Bacteriological Quality of the Water

Biological water quality analysis was done using multiple tube method for faecal indicators, which is a group of organisms that indicates the presence of faecal contamination, therefore this study only infers that pathogens may be present. The presence coliform bacteria was determined in three stages which are presumptive test, confirmed test and completed test.

The Most Probable Number (MPN) of coliforms present in the water was determined by the number of positive tubes in reference to the table of computation of MPN according to the standard methods for the examination of Water and waste water (APHA, 2005). A hundred time's dilution of original water sample was done and thus the same factor was used to calculate the counts of MPN per 100 ml of sample and 95% confidence limit for various combinations of (five 10-ml, five 1-ml and 0.1-ml) samples used. There were no coliforms found in the treated water during the dry and wet season, which indicates the effectiveness of the water treatment method in place in removal of micro-organisms. This is unlike the raw water which had coliforms during dry and the wet season.

4.2.1 Results of Most Probable Number (MPN) of coliforms

The indicator micro-organisms were found in the rivers and the raw water storage reservoir in both dry and the wet season were as presented in Figure 4.8 and appendix 3.

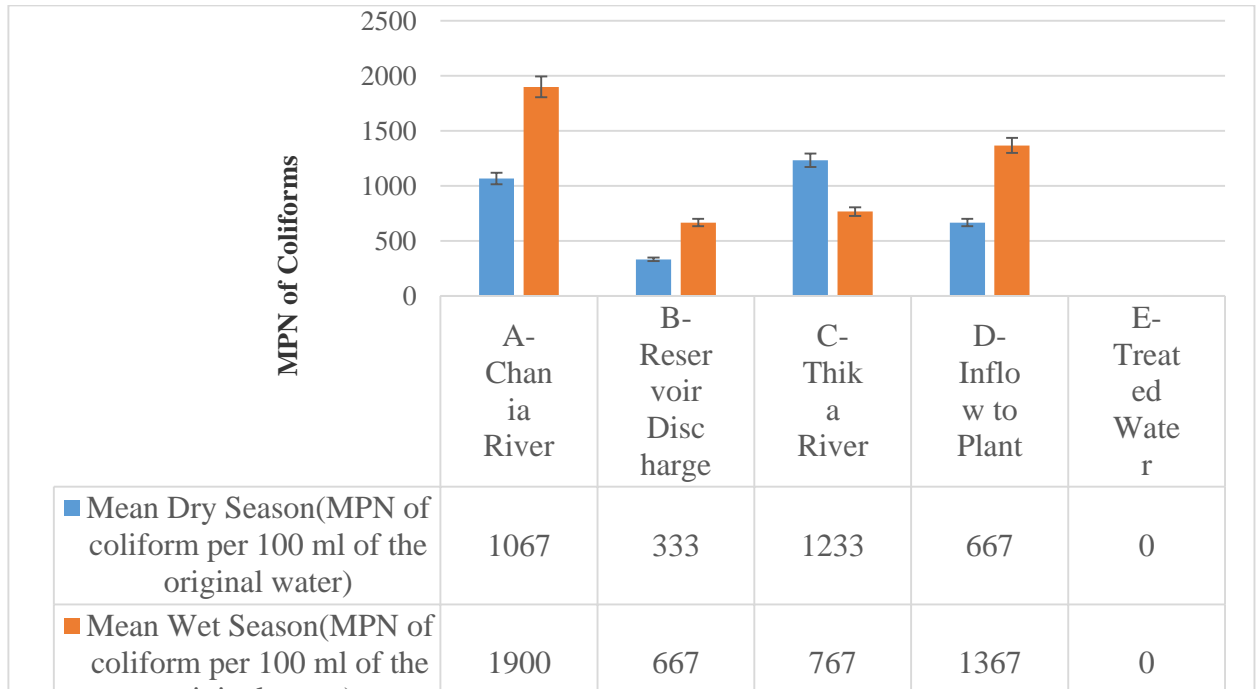


Figure 4.8: MPN of coliforms

The highest number of Most Probable Number of Coliforms was 1900 ± 624 , recorded at Chania River sampling point during the wet season while the lowest was 333 ± 115 recorded at the Thika reservoir discharge during the dry season.

Coliforms were found in the Catchment Rivers and the reservoir during the two seasons which is a major indicator of faecal contamination. This is evidence of pollution associated with faecal contamination from man or other warm-blooded animals. It may be accompanied by pathogens, but may not necessarily those that cause diseases.

Therefore the findings of this study established that there is faecal contamination of water in the catchment because coliforms are found only in the mammalian intestinal tract (WHO, 2011). This contamination is likely to be as a result of raw sewage getting into the river system or wastes from domestic animals.

4.3 Heavy Metals Concentration in Chania Catchment

The determination of heavy metals in water samples was done using Total X-ray Fluorescence spectroscopy (TXRF). The heavy metals that were detected in the water include the following; Lead, Chromium, Manganese, Iron, Nickel, Copper, Zinc, Potassium, and Calcium. Appendix 2 and Figures 4.9 and 4.10 show the mean concentrations of the heavy metals at various sampling locations during the dry and wet season.

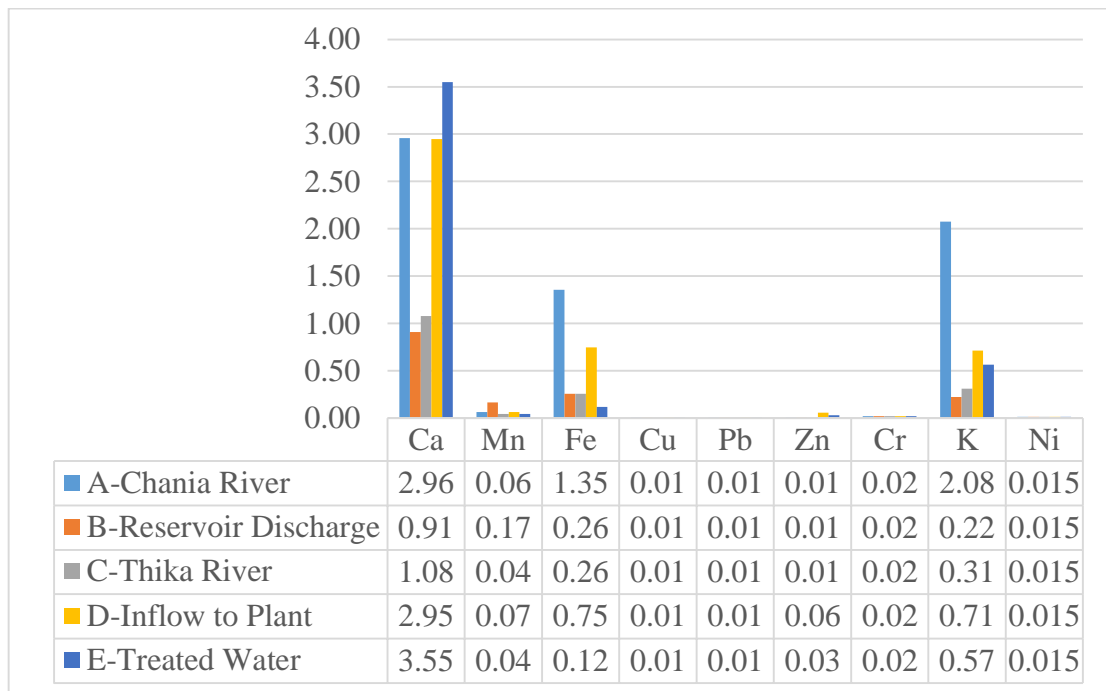


Figure 4.9: Mean concentration of heavy metals during the dry season

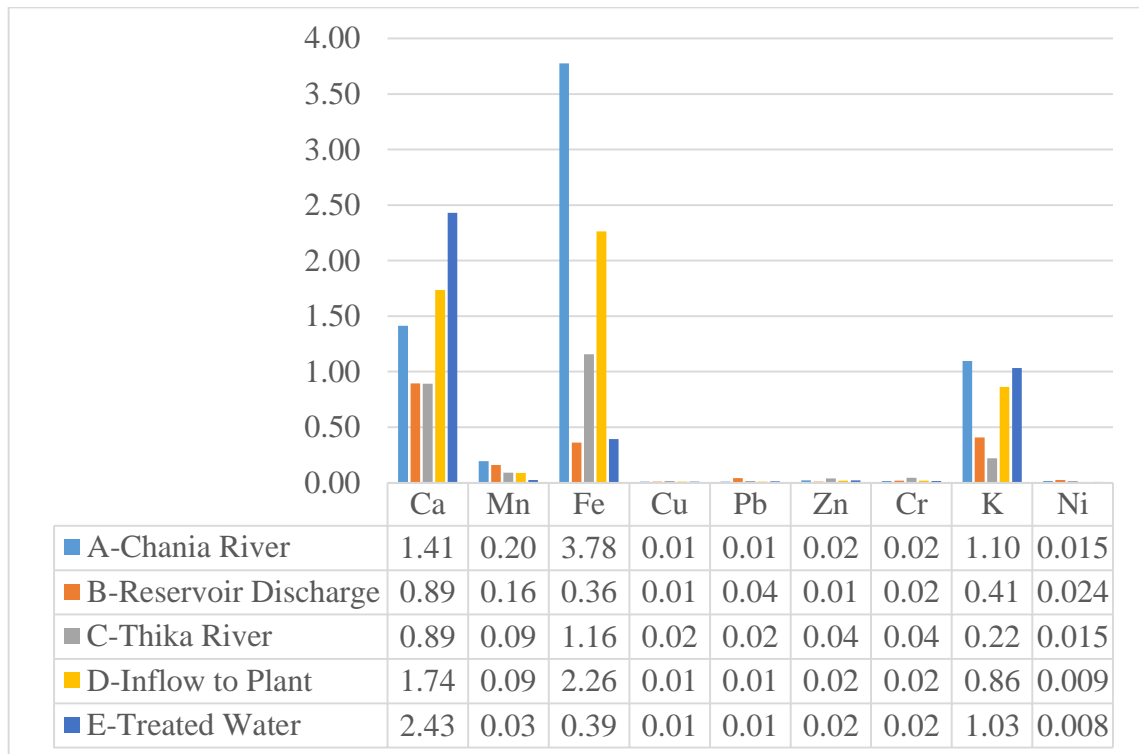


Figure 4.10: Mean concentration of heavy metals during the wet season

The mean concentration of the heavy metals that were found to be above the recommended maximum contaminant levels (MCL) and showed statistically significant differences between dry and wet seasons at the various sampling points were as presented here.

4.3.1 Manganese (Mn)

The mean concentration of Manganese was found as presented in Figure 4.11 and Appendix 2. The mean concentration of manganese in Thika reservoir were found to be above the recommended maximum concentration level of 0.1mg/L during both dry and wet seasons .i.e. (0.17 ± 0.01 mg/L) and wet season (0.16 ± 0.04 mg/L) respectively. Chania River dry and wet season mean Mn concentration was 0.06 ± 0.01 mg/L and 0.20 ± 0.03 mg/L respectively showing elevation above recommended level during the wet season only.

Mean concentration of manganese in treated water during dry and wet seasons was 0.04 ± 0.01 mg/L and 0.03 ± 0.01 mg/L respectively which was within WHO standard.

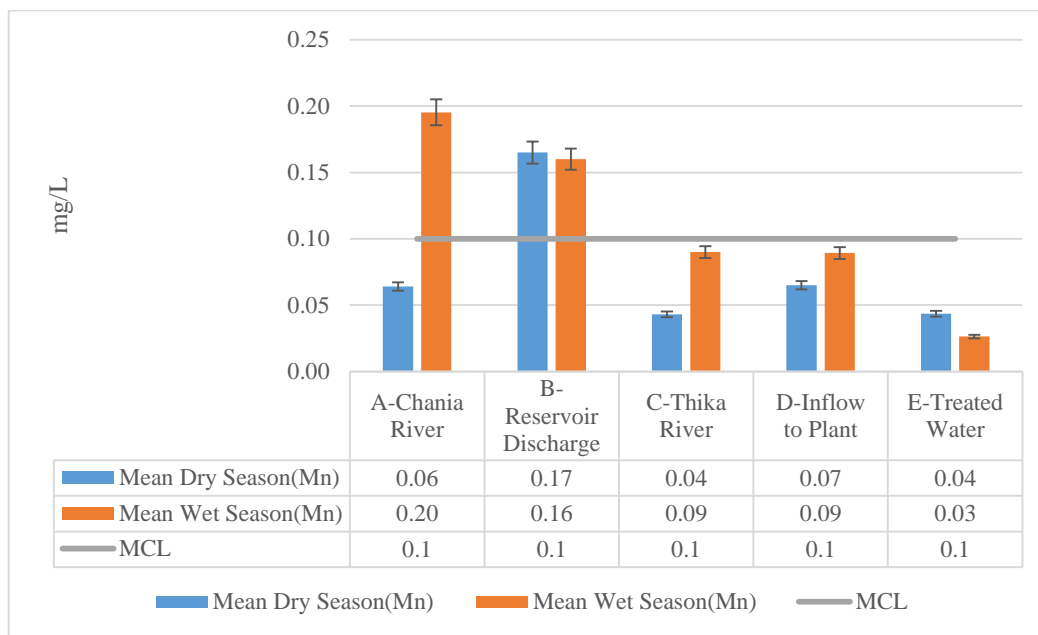


Figure 4.11: Concentration of Manganese during wet and dry seasons

The t-test results at 95% confidence level indicated that there was a statistically significant difference in the concentration of Manganese in Chania river between the dry and wet seasons where; ($t_{cal} = 7.668$, $t_{tab} = 2.776$, $d.f = 4$, $P = 0.05$) but not in Thika River and reservoir discharge where; ($t_{cal} = 1.729$, $t_{tab} = 2.776$, $d.f = 4$, $P = 0.05$ and $t_{cal} = 0.420$, $t_{tab} = 2.776$, $d.f = 4$, $P = 0.05$) respectively. Treated water also showed no statistically significant difference in mean manganese concentration where; ($t_{cal} = 1.225$, $t_{tab} = 2.776$, $d.f = 4$, $P = 0.05$) and the mean concentration of manganese in treated water was found to be within recommended level during both dry and wet seasons.

Manganese is one of the most common elements in the earth’s crust and as water percolates through soil and rock it can be dissolved then transported into the rivers through sub-surface flow. Manganese is also a key constituent element in tea leaves and there is likelihood that decayed tea vegetation contribute to the high concentration levels found

the water. Thus the likelihood that the mineral is washed into the river from the soils in the catchment during the wet season and is accumulating in Thika reservoir whose main feeder river is Thika River. At levels exceeding 0.1 mg/L, manganese in water supplies causes an undesirable taste in beverages and stains sanitary ware and laundry (WHO, 2011).

4.3.2 Iron (Fe)

The highest mean concentration of iron in the catchment during the wet and dry seasons was recorded at Chania River with mean iron concentration of 3.78 ± 0.17 mg/L and 1.35 ± 0.01 mg/L respectively. Mean concentration of iron in Thika River during the dry and wet season was 0.26 ± 0.07 mg/L and 1.16 ± 0.17 mg/L while that from the reservoir discharge was 0.26 ± 0.09 mg/L and 0.36 ± 0.08 mg/L respectively.

At 95% confidence level, the *t-test* results indicated that there was a significant difference between the wet and the dry season iron concentration in Chania River and Thika River where; ($t_{cal} = 24.7$, $t_{tab} = 2.776$, $d.f = 4$, $P = 0.05$ and $t_{cal} = 8.479$, $t_{tab} = 2.776$, $d.f = 4$, $P = 0.05$) respectively. However, there was no observed significant difference between dry & wet season concentration level of iron from reservoir discharge where; ($t_{cal} = 1.438$, $t_{tab} = 2.776$, $d.f = 4$, $P = 0.05$).

Mean concentration levels of Fe in the treated water during dry and wet season was 0.12 ± 0.02 mg/L and 0.39 ± 0.12 mg/L respectively, showing iron levels in treated water during the wet season being above the recommended maximum concentration of 0.3 mg/L. The *t-test* indicated that there was a significant difference between dry and wet season means of Fe levels in treated water where; ($t_{cal} = 3.84$, $t_{tab} = 2.776$, $d.f = 4$, $P = 0.05$). The mean Fe values were as presented in Figure 4.12 in Appendix 2.

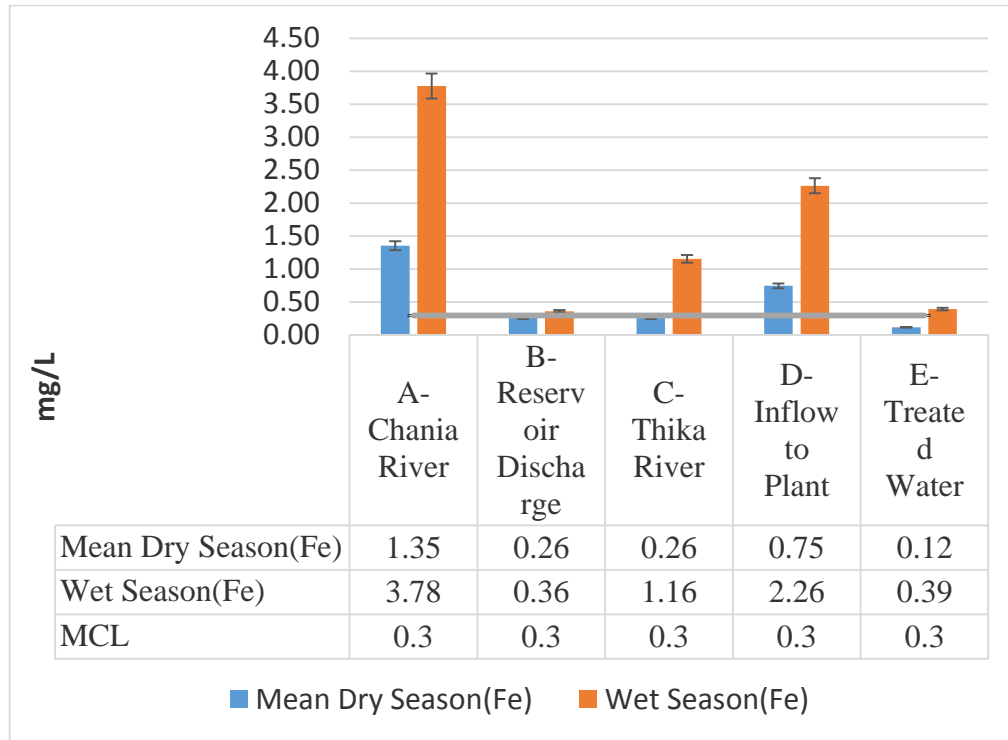


Figure 4.12: Concentration of Iron during wet and dry seasons

Weathering processes release elemental iron into surface waters especially during the rains and dissolution of iron can occur as a result of oxidation and decrease in pH. The iron concentration during the wet season was found to be higher than the dry season and can be attributed to soil geology and weathering from rocks and run off from quarry mining sites. The storage facility iron may be resulting accumulation of iron precipitates. Iron promotes the growth of “iron bacteria”, which derive their energy from the oxidation of ferrous iron to ferric iron and in the process deposit a slimy coating on piping. At levels above 0.3mg/L, iron stains laundry, may cause colour and turbidity to develop but usually has no noticeable taste at iron concentrations below 0.3 mg/L (WHO, 2011).

4.3.3 Copper

Copper levels within the catchment were found to be within the required standards, i.e. below 0.05 mg/L which is the recommended NEMA standard (WHO level is < 2.0mg/L). The highest level of copper was found in Thika River, 0.02 mg/L.

At 95% confidence level, the *t-test* results indicated that there was a significant difference between dry and wet season means from Thika River where; ($t_{cal}=6.124$, $t_{tab}=2.776$, $d.f = 4$, $P=0.05$). The likely source of copper in source water is from residuals of chemical fungicides applied on farmlands to control pests that are later washed from agricultural land by rain during the wet season. Copper level in treated water was found to be within the allowable contaminant level. The mean copper concentration levels were as presented in Figure 4.13 in Appendix 2.

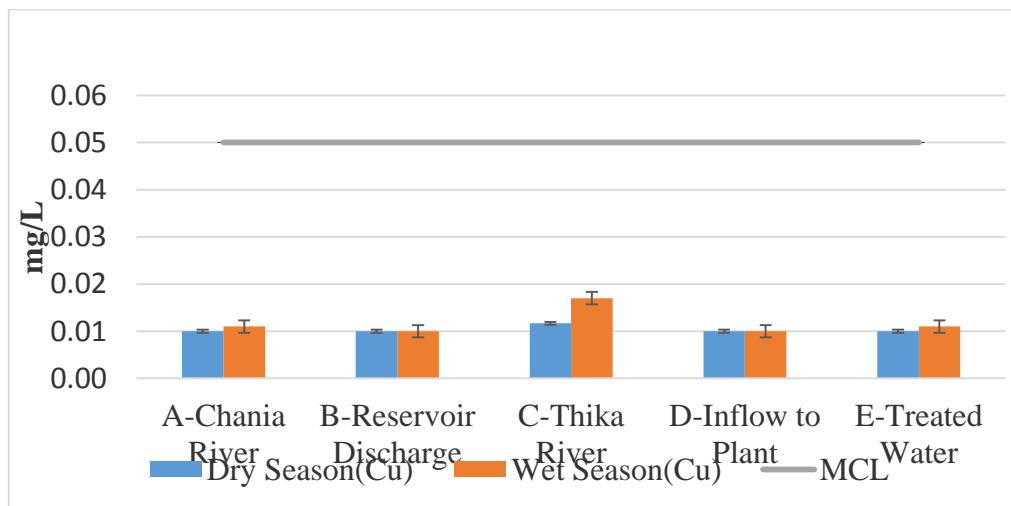


Figure 4.13: Mean concentration of Copper during wet and dry seasons

4.3.4 Lead

The mean lead concentration levels in the catchment during the wet season were found to be above 0.01 mg/L which is the WHO recommended standard at the Thika reservoir discharge and Thika river sampling points with the highest level being recorded in Thika reservoir discharge point of 0.04 ± 0.01 mg/L. During the dry season, mean lead concentration levels were below 0.01 mg/L however, Chania River sampling point had mean lead concentration level that below 0.01 mg/L during both dry and wet seasons.

The mean lead concentration levels were as presented in Figure 4.14 in Appendix 2.

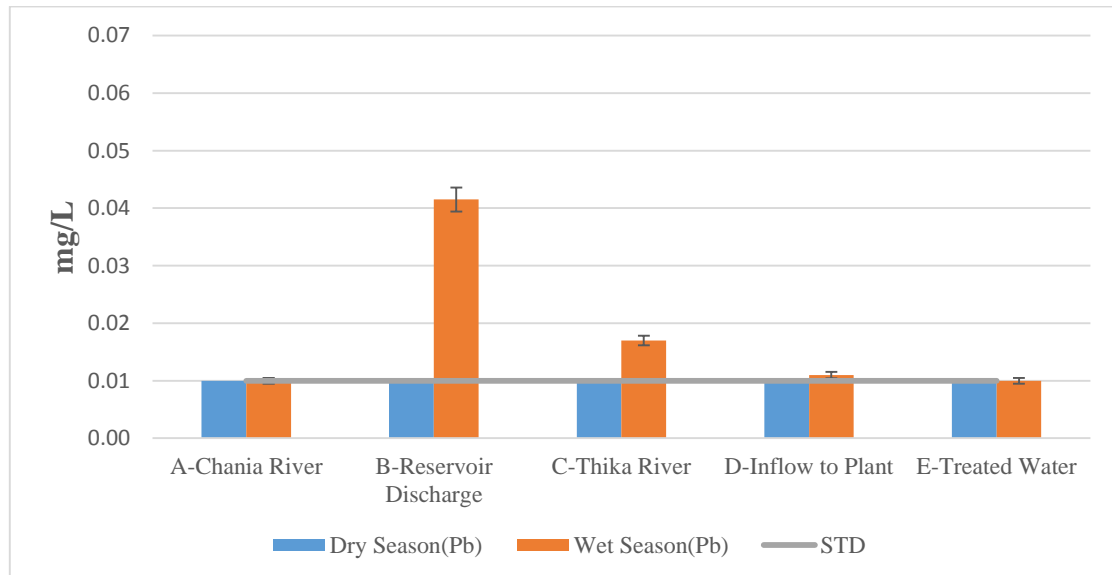


Figure 4.14: Concentration of Lead during wet and dry seasons

Lead is likely to be accumulating in Thika reservoir emanating from Thika River and its catchment which recorded a mean lead level of 0.04 ± 0.01 mg/L during the wet season. Treated water recorded mean lead concentration of 0.01 ± 0.00 mg/L during the wet season which was just within the recommended levels. Kenya National Environmental Management Authority (NEMA) guidelines requires lead concentration (maximum allowable) to be 0.05 mg/L for all sources of domestic water, which is five times lower than the WHO value, therefore the sources would be deemed to comply. The likely sources

in the catchment is run-off from car garages where lead-acid batteries are disposed and from vehicle alloy paint wastes.

4.3.5 Zinc

The highest mean concentration of Zinc in the catchment during the wet and dry seasons were 0.06 ± 0.01 mg/L and 0.04 ± 0.02 mg/L respectively both recorded at Thika River sampling point and were below maximum contaminant levels allowed of 1.5 mg/L. At 95% confidence level, the *t-test* results indicated that there was no statistically significant difference between dry & wet season means from Thika river where; ($t_{cal} = 1.549$, $t_{tab} = 2.776$, $d.f = 4$, $P=0.05$).

Mean Zinc concentration in treated water during dry and wet seasons was 0.03 ± 0.00 mg/L and 0.02 ± 0.00 mg/L respectively. At 95% confidence level, the *t-test* results indicated that there was a statistically significant difference between dry and wet season means where; ($t_{cal} = 17.62$, $t_{tab} = 2.78$, $d.f = 4$, $P=0.05$). The mean zinc concentration levels were as presented in Appendix 2.

4.3.6 Chromium

The mean concentration of Chromium in the catchment was found to be below 0.02 mg/L during the dry and wet seasons except in Thika river sampling point where the mean concentration level of 0.045 ± 0.001 mg/L was recorded during the wet season. The WHO allowable maximum for chromium level is 0.05 mg/L.

The mean Chromium concentration levels were as presented in Appendix 2 for both dry and wet seasons. The likely source of chromium within the catchment could be as a result of fluid effluent and run-off water arising from motor vehicle garages in the upstream part of catchment.

4.3.7 Nickel

The mean concentration of Nickel in Thika reservoir were found to be 0.02 ± 0.01 mg/L during the wet season, which is slightly above the recommended WHO concentration level

of 0.02 mg/L. All the other sampling points recorded concentrations below 0.02 mg/L during both dry and wet seasons.

These result indicate that there is a likelihood that nickel, which is normally a constituents of inks, dyes and paints could be accumulating in Thika reservoir. The main source of nickel in the catchment would be likely the run-off from pollution sources upstream of Thika reservoir i.e. vehicle garages using nickel based paints. The mean nickel concentration levels were as presented in appendix 2.

4.3.8 Sodium

Figure 4.15 and appendix 1 shows the concentration of sodium ions in the catchment and in treated water as established during this study.

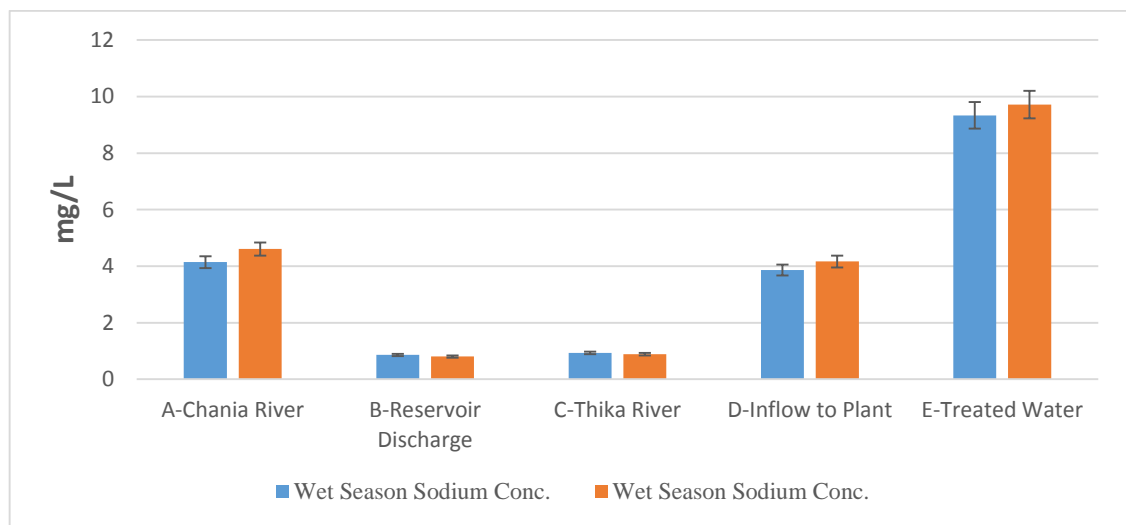


Figure 4.15: Concentration of Sodium during wet and dry seasons

The highest mean concentration of sodium in the catchment was 4.61 ± 0.36 mg/L recorded at Chania River during the wet season and the lowest recorded mean concentration was 0.93 ± 0.004 mg/L during the dry season recorded at Thika River. The sodium concentration in the treated water clear well was highest at within a range of 9.32 – 9.37 mg/L and 9.69 - 9.78 mg/L during the dry and wet seasons respectively.

At 95% confidence level, the *t-test* results indicated that there was a significant difference between the wet and the dry season sodium concentration in Thika River where; (t_{cal}

=6.433, $t_{tab}=2.776$, $d.f = 4$, $P=0.05$). However, there was no statistically significant difference in concentration of sodium in Chania river between the dry and wet seasons where; ($t_{cal}=2.240$, $t_{tab}=2.776$, $P=0.05$, $d.f = 4$). The mean concentration of sodium from reservoir discharge between dry season and wet season showed a significant difference between the wet and the dry season sodium concentration where; ($t_{cal}=2.882$, $t_{tab}=2.776$, $d.f = 4$, $P=0.05$).

There was a statistically significant difference in concentration of sodium in in the treated between the dry and wet seasons where; ($t_{cal}=10.407$, $t_{tab}=2.776$, $d.f = 4$, $P=0.05$). The higher level of sodium concentration is attributed to the residual water treatment chemicals (usually Sodium Carbonate) added during water treatment process to adjust the pH to drinking water standards.

However, the concentration levels of sodium were generally within the WHO recommended levels for drinking water of below 200 mg/L (WHO, 2011).

4.3.9 Aluminium

Figure 4.16 and appendix 1 illustrates the mean concentration of Aluminium in the catchment and in treated water as established during this study.

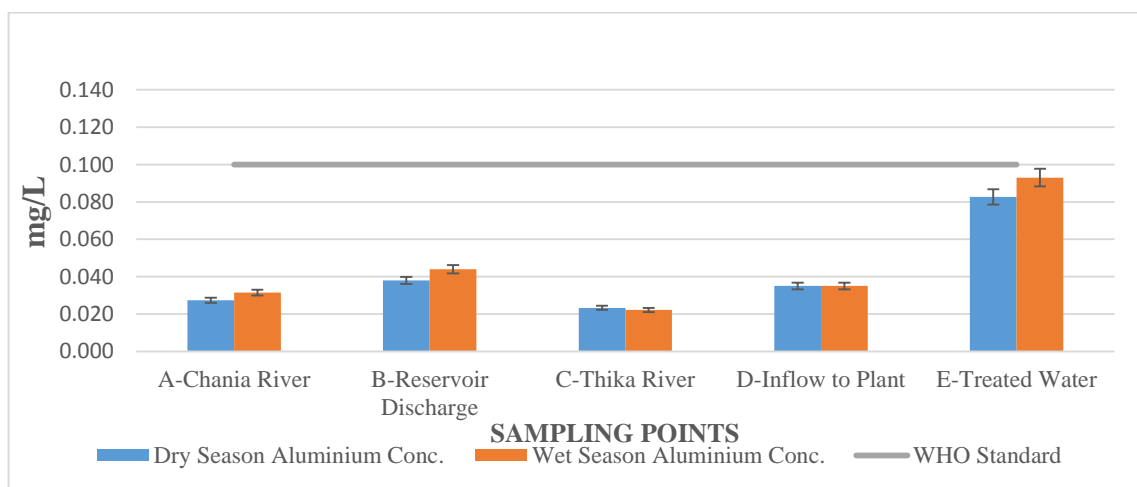


Figure 4.16: Concentration of Aluminium during wet and dry seasons

The mean concentration of Aluminium in the catchment was found to be below 0.05 mg/L with a range of 0.01 – 0.05 mg/L which was within the WHO recommended level of below 0.10 mg/L. The highest mean concentration in the catchment was 0.044 ± 0.010 mg/L recorded at the reservoir discharge during the wet season while the dry season, the highest concentration was 0.038 ± 0.011 mg/L at the same reservoir discharge sampling point. The lowest mean concentration of Aluminium was 0.023 ± 0.005 mg/L recorded at Thika River sampling point during the dry season. The mean concentration at the treated water clear well during dry and wet seasons was recorded as 0.083 ± 0.013 mg/L and 0.093 ± 0.012 mg/L respectively.

The mean concentration of aluminium in the treated water clear well during the wet season ranged from 0.077 – 0.112 mg/L during the wet season and 0.067 – 0.098 mg/L during the dry season which was within the recommended level.

The *t-test* results at 95% confidence level indicated that there was no significance difference in concentration of Aluminium between the dry and dry seasons at Chania River and Thika River where; ($t_{cal}=0.900$, $t_{tab}=2.228$, $d.f=10$, $P=0.05$ and $t_{cal}=0.219$, $t_{tab}=2.228$, $d.f=10$, $P=0.05$) respectively. There was also no significance difference in concentration of Aluminium from the reservoir discharge between the wet seasons where; ($t_{cal}=0.989$, $t_{tab}=2.228$, $d.f=10$, $P=0.05$). The *t-test* results at 95% confidence level also indicated no significant difference in concentration of Aluminium in the treated water between the wet seasons where; ($t_{cal}=1.385$, $t_{tab}=2.228$, $d.f=10$, $P=0.05$).

The higher Aluminium concentration in the treated water can be attributed to coagulant chemicals used for water treatment, usually aluminium sulphate. Dissolved aluminium concentrations in natural waters with near-neutral pH values usually range from 0.001 to 0.05 mg/L but rise to 0.5–1.0mg/L in more acidic waters or water rich in organic matter (WHO, 1997). Residual aluminum in treated water is undesirable for aesthetic reasons, but also because of a possible link between aluminum and adverse neurological effects such as Alzheimer's disease.

4.4 Nutrients Concentrations in Chania Catchment

Nutrients analysis was done for Phosphate and Nitrate.

4.4.1 Nitrates in Chania Catchment

The figure 4.17 and Appendix 1 illustrates mean concentration of Nitrates (NO_3) in different sampling points during wet and dry season.

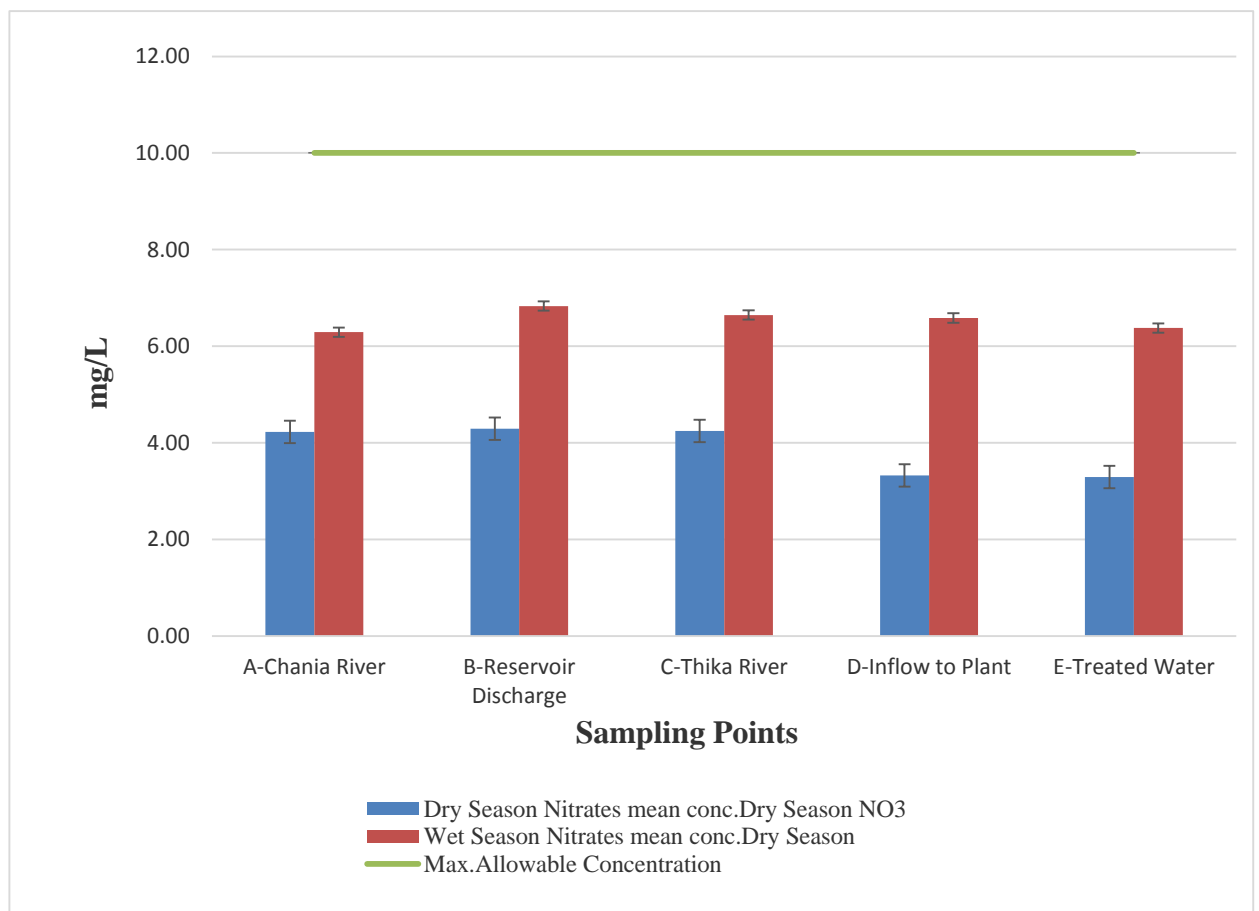


Figure 4.17: Concentration of Nitrates during wet and dry seasons

The mean concentration of nitrates was found to be within the recommended WHO concentration level in all sampling points during both wet and dry season. During the wet season, the highest mean concentration was 6.83 ± 0.60 mg/L recorded at the reservoir discharge sampling point; this was also the sampling point that recorded the highest mean

concentration during the dry season of 4.29 ± 0.31 mg/L. Chania River recorded and the lowest mean concentration during both the wet and dry seasons of 6.29 ± 0.52 and 4.23 ± 0.21 mg/L respectively.

The mean concentration of Nitrate in the catchment ranged from 5.76 – 7.43 mg/L during the wet season while during the dry season it ranged from 6.23 – 7.43 mg/L. In the reservoir discharge, the mean concentration ranged from 3.98 – 4.60 mg/L during the wet season and 4.28 – 4.30 mg/L during the dry season. The mean concentration from the treated water clear well during the wet season ranged from 5.77 – 6.99 mg/L during the wet season and 3.05 – 3.53 mg/L during the dry season.

The *t-test* results at 95% confidence level, indicated that there was significant difference in concentration of nitrates between the wet and dry season at Chania river and Thika river sampling points where; ($t_{cal} = 8.998$, $t_{tab} = 2.228$, $d.f = 10$, $P = 0.05$ and $t_{cal} = 14.171$, $t_{tab} = 2.228$, $d.f = 10$, $P = 0.05$) respectively. The reservoir discharge also showed a significant difference in the concentration of nitrate between the wet and dry season where; ($t_{cal} = 9.213$, $t_{tab} = 2.228$, $d.f = 10$, $P = 0.05$). The treated water from the clear well also indicated a significant difference in nitrate concentration between the wet and dry season where; ($t_{cal} = 11.547$, $t_{tab} = 2.228$, $d.f = 10$, $P = 0.05$).

From Figure 4.18, it can be observed that the concentration of nitrates was higher during the wet season than in the dry season. There was negligible removal of nitrates after the treatment process. This can be attributed to flow of soil sediments mixed with fertilizers and domestic waste such as organic manure used on the agricultural farms adjacent to the rivers during the wet season. Most of the farmlands in the catchment have extensive tea bushes with horticultural crops along the river riparian.

4.4.2 Phosphates in Chania Catchment

The mean phosphates concentration levels were as presented in Figure 4.18 in appendix 1 in the different sampling points during wet and dry season.

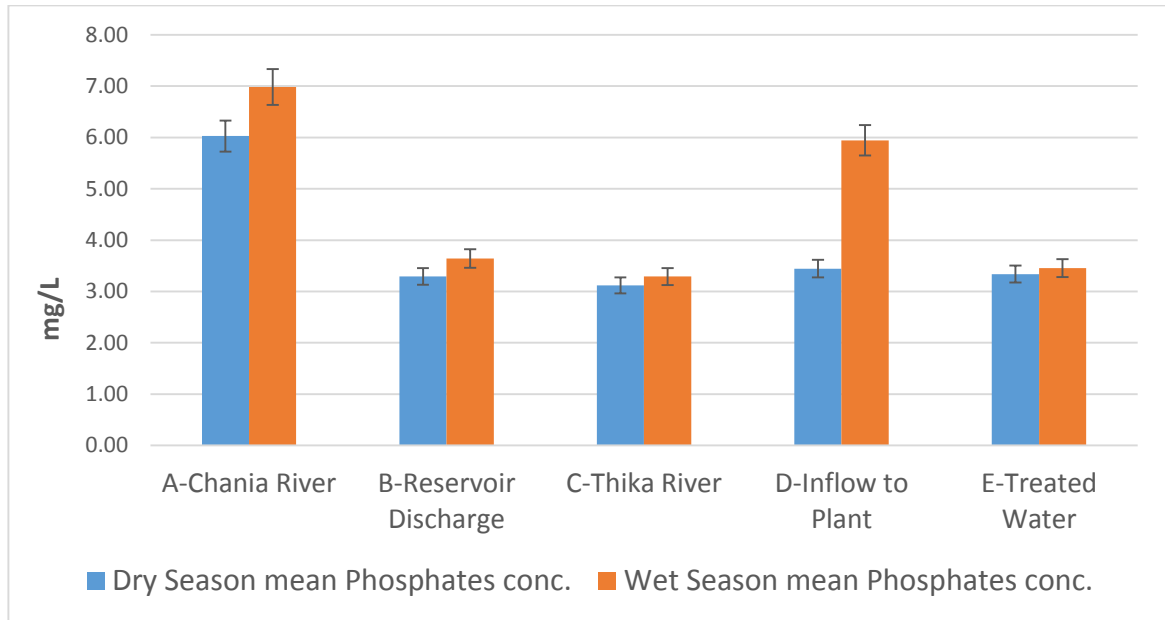


Figure 4.18: Concentration of Phosphates during wet and dry seasons

The mean phosphates concentration was found to be above the WHO recommended standard of 0.5 mg/L in all sampling points during both wet and dry season. During the wet season, the highest mean concentration was 6.98 ± 0.68 mg/L at Chania River sampling point and the lowest was 2.17 ± 0.11 mg/L at Thika River. During the dry season, the highest concentration level was found to be 6.03 ± 0.47 mg/L at Chania River while the lowest was 3.12 ± 0.63 mg/L at Thika River sampling point. The mean concentration of phosphate in the catchment ranged from 2.07 – 7.67 mg/L during the wet season while during the dry season it ranged from 2.10 - 6.51 mg/L. In the reservoir discharge, the mean concentration ranged from 3.03 - 4.23 mg/L during the wet season and 2.83 – 3.74 mg/L during the dry season.

The mean concentration of phosphate in the treated water during the wet season ranged from 2.59 – 4.23 mg/L during the wet season and 3.23 - 3.43 mg/L during the dry season. The phosphate concentration in the raw water entering the water treatment plant during the wet season was 5.94 ± 0.27 mg/L, thus an appreciable phosphates removal during the

wet season was observed. The mean concentration of phosphate in the catchment during the dry and wet seasons was found to be 4.57 mg/L and 5.14 mg/L respectively.

The *t-test* results at 95% confidence level, indicated that there was a significant difference in concentration of phosphates between the wet and dry season in Chania river and Thika river where; ($t_{cal}=2.815$, $t_{tab}=2.228$, $d.f=10$, $P=0.05$ and $t_{cal}=2.904$, $t_{tab}=2.228$, $d.f=10$, $P=0.05$) respectively. But there was no significant difference was observed in reservoir discharge sampling point where; ($t_{cal}=0.610$, $t_{tab}=2.228$, $d.f=10$, $P=0.05$). The *t-test* results for the treated water also indicated that there was no significance difference in concentration of phosphates between the wet and dry season where; ($t_{cal}=0.197$, $t_{tab}=2.228$, $P=0.05$, $d.f=10$).

In this study, Chania River sampling point consistently indicated the highest concentration levels of phosphates for both dry and wet seasons. This is the point where there are extensive tea plantations on the lower part of the catchment hillsides while the upper parts have horticultural farming activities going on. The phosphates could likely be as a result of phosphate fertilizers applied on the farms.

There were elevated levels of phosphates, in both dry and wet seasons. High levels of phosphates suggest likely sewer discharge and phosphorus based detergents effluent into the rivers. Orthophosphates may result from agricultural wastes such as residual phosphate fertilizers applied on farms, phosphate rich rocks that may release phosphorus during weathering and erosion. Water reservoirs such as Thika Reservoir serve as phosphorus sinks, where particles containing phosphorus settle and are covered with sediment with substrate re-introduced to the water after discharge.

4.5 Chloride

Figure 4.19 and appendix 1 shows the mean concentration of chloride ions in the catchment as established during this study.

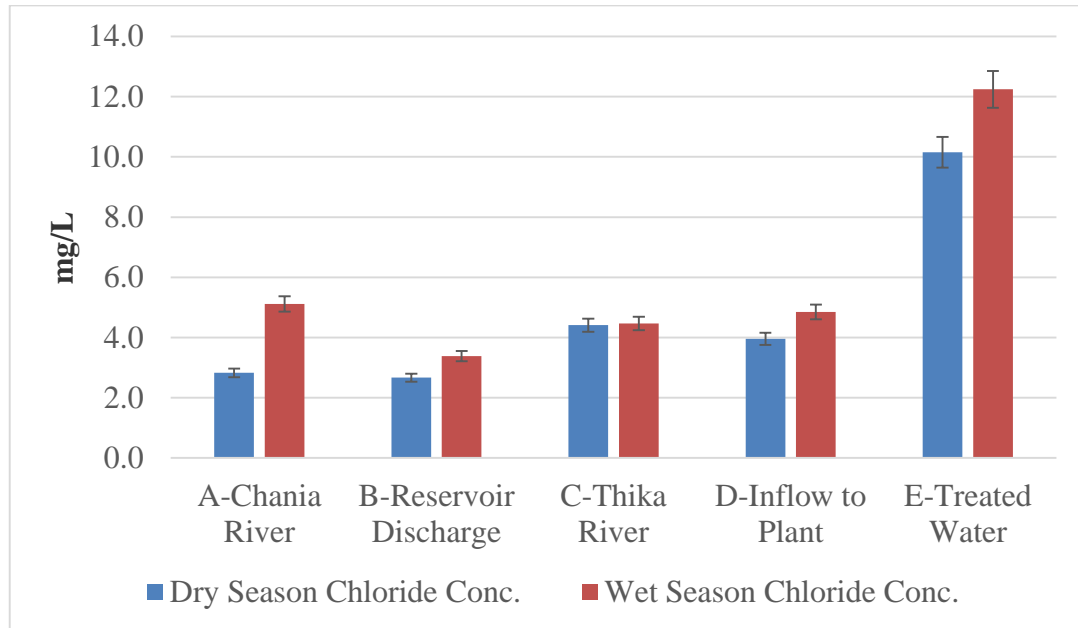


Figure 4.19: Concentration of Chloride during wet and dry seasons

The mean chloride concentration in the catchment was found to be low during both wet and dry seasons (<10.0 mg/L) and consistent with experience from surface water sources.

During the wet season, the highest mean concentration of Chloride ions was 5.11 ± 0.72 mg/L at Chania River sampling point and the lowest was 3.38 ± 0.33 mg/L at Thika reservoir discharge sampling point. During the dry season, the highest concentration level was found to be 4.41 ± 0.61 mg/L at Thika River while the lowest was 2.67 ± 0.36 mg/L at Thika Reservoir sampling point.

The *t-test* results at 95% confidence level, indicated that there was significant difference in concentration of Chloride ions between the wet and dry season at Chania river and Thika river sampling points where; ($t_{cal} = 5.038$, $t_{tab} = 2.228$, $d.f = 10$, $P = 0.05$ and $t_{cal} = 2.518$, $t_{tab} = 2.228$, $d.f = 10$, $P = 0.05$) respectively. The reservoir discharge also showed no significant difference in the concentration of Chloride ions between the wet and dry season where; ($t_{cal} = 0.1339$, $t_{tab} = 2.228$, $d.f = 10$, $P = 0.05$). The treated water from the clear well also indicated no significant difference in concentration of Chloride ions between the wet and dry season where; ($t_{cal} = 1.558$, $t_{tab} = 2.228$, $d.f = 10$, $P = 0.05$).

High levels of Chloride which give a salty taste in drinking-water are usually associated with ground water sources and saline intrusion. Chlorinated drinking water often increases chloride levels as can be observed from the results with highest concentration level found during wet season of 12.24 ± 1.87 mg/L. Concentrations of chloride (Cl^-) in excess of 250 mg/L are increasingly likely to be detected by taste (WHO, 2011). Excessive chloride concentration is known to increase rates of corrosion of metals in the distribution system (WHO, 2011) depending on the alkalinity of the water.

4.6 Free Residual Chlorine

Appendix 1 show the mean concentration of Free Residual Chlorine (FRC) in treated water storage reservoir as established during this study.

The mean concentration of FRC in the treated water at the water works during the dry and wet season ranged from 1.10 - 1.40 mg/ and 1.0 - 1.30 mg/L respectively. The *t-test* results at 95% confidence level, indicated that there was a significant difference in concentration of FRC between the wet and dry season where; ($t_{cal}=2.441$, $t_{tab}=2.228$, $d.f=10$, $P=0.05$).

The health based guideline value for free chlorine in drinking-water is 5.0 mg/L (WHO, 1996). The U.S. Environmental Protection Agency's Drinking Water Criteria for Chlorine (US EPA 1994) gives a federal standard of 4.0 mg/L for chlorine in drinking water known as a Maximum Residual Disinfectant Level (MRDL) which is a level of a disinfectant added for water treatment that may not be exceeded at the consumer's tap without an unacceptable possibility of adverse health effects. According to the Kenya Standards for Drinking Water Quality (KES KS 05-459, 1996) the recommended residual concentration level at the consumer tap is between 0.2 – 0.5 mg/L.

4.7 Rainfall amounts in the Catchment

Figure 4.20 depicts the annual mean cumulative rainfall for the period 2012 to 2015 from two Kenya Meteorological Department (KMD) stations within the Chania Sub-

Catchment. These are Sasumua Dam Rainfall Station (KMD Code: 9036188) and Thika Dam Rainfall Station (KMD Code: 9036344).

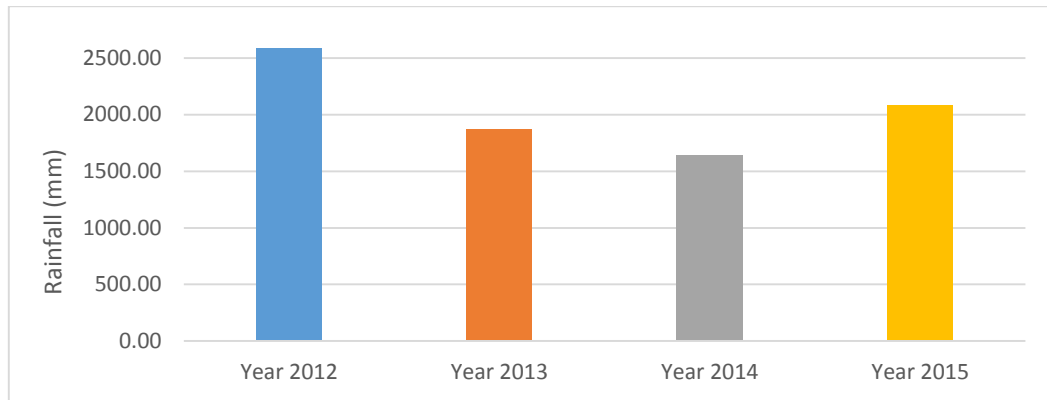


Figure 4.20: Annual cumulative rainfall in Chania Sub-Catchment (2012 – 2015)

Figure 4.21 shows the mean monthly cumulative rainfall trend for the same period 2012 to 2015. Generally, the year of study (2015) showed normal seasonal trend in rainfall compared with the previous three years. As highlighted from literature review in the background to this study on page 3, Chania catchment is part of the Aberdares highlands and generally has a bimodal rainfall pattern as a result of the inter-tropical convergence zone. The two distinct rain seasons are fairly well distributed in the months of March to June and September to December and on average the area receives about 2,000 mm of rainfall.

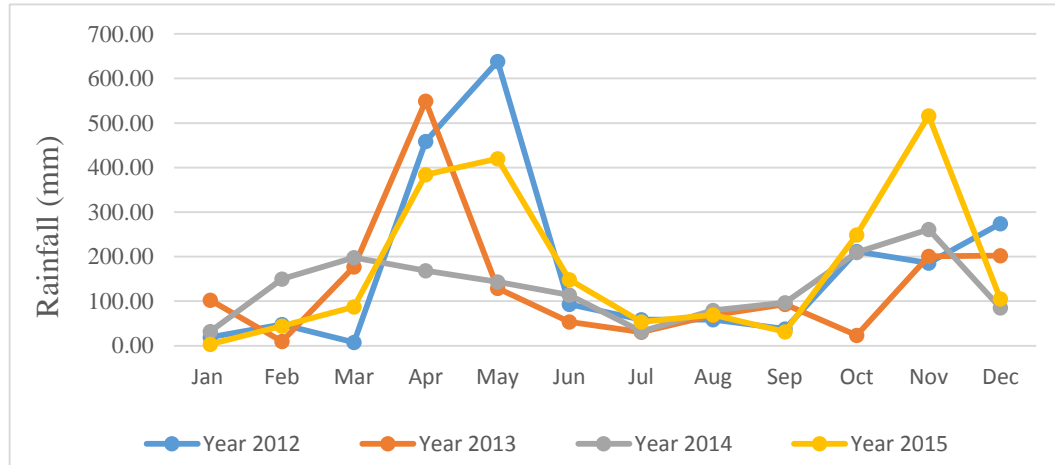


Figure 4.21: Monthly mean cumulative rainfall Chania Sub-Catchment (2012 – 2015)

The the mean cumulative rainfall in the dry season months of July – September was 50.1 mm while that of the wet season in October – December was 290.0 mm.

The wet season recorded the highest turbidity of 107.89 ± 5.85 NTU in the catchment as a result of the rainfall experienced, attributed to run-off with probable soil erosion from farmland and hillsides considering the steep terrain in the area. The dry season had low rainfall and highest mean turbidity was 33.00 NTU. Rainfall therefore influenced the physical, chemical and biological pollution level of the water within the catchment as the wet season showed higher elevations of contaminants than the dry season.

4.8 Activities in Chania Catchment

Agriculture is the dominant source of livelihood in Chania Catchment and being situated in the highlands has tea as a major cash crop followed by horticulture and livestock keeping. The relatively cool climate coupled with alternating wet and dry seasons is favourable for highland agriculture. There is intensive land utilization in the tea crop which covers most of available land and dairy cattle rearing, both range and zero grazing.

As highlighted on Plates 3.1 and 3.6, Thika River and Chania river banks respectively show agricultural crops such as maize, bananas and cabbages being grown on the river banks without any buffer crop such as nappier to hold the soils. Plate 4.5 also illustrates maize growing along Chania river riparian and tea crop on the hillsides.



Plate 4.6: Farming activities along Thika River a few metres upstream of sampling point B

Plate 4.6 shows the horticultural activities (vegetables) and domestic animals, sheep and cattle grazing along river plain with tea bushes on the higher areas. Other crops grown include pulses (e.g. beans), root and tuber crops (potatoes), and horticultural crops (vegetables and fruits). Horticultural crops are grown on small portions on the valley bottoms near the rivers.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This study demonstrates that pollution effects of natural and anthropogenic activities within the Chania catchment are prevalent. The study aimed at establishing the quality of surface water in Chania catchment through analyzing the bacteriological and Physico-chemical quality of the water during the wet and dry season. The objectives of this study were achieved.

The microbiological quality of the surface water was found to contain a high number microbial indicator counts which were considered in excess of WHO recommended guidelines for drinking water (WHO, 2011). This implies that, water from these sources is not suitable for drinking without treatment. Generally, most of the physico-chemical parameters were within the allowable WHO maximum contaminant levels with the exception of wet season. The results of both TDS and EC recorded at Thika River were low during the wet season and high during the dry season which was a different observation comparing with the other sampling points. Mean dry season EC concentration level recorded at Thika River was 53.10 ± 2.65 $\mu\text{S}/\text{cm}$ and wet season level was 16.64 ± 0.40 $\mu\text{S}/\text{cm}$ while the dry and wet season TDS levels for the same sampling point were 34.52 ± 1.15 mg/L and 10.90 ± 0.37 mg/L respectively. Further scrutiny showed that Thika River had higher levels of heavy metal pollutants Zinc, lead and chromium emanating from the catchment than other sampling points. It can therefore be inferred that higher flow volumes and low turbidity in river Thika cause pollution dilution effects during the wet season.

Analysis of the surface water for heavy metals revealed that water was polluted with manganese, iron, nickel and lead but chromium, copper, zinc, potassium, arsenic, vanadium and calcium were below the WHO maximum allowable limits. The concentration of iron, manganese and Nickel were highest during the wet season in catchment.

The highest mean concentration of iron in the catchment during the wet and dry seasons was recorded at Chania River with mean concentration of 3.78 ± 0.17 mg/L and 1.35 ± 0.01 mg/L respectively. After treatment, the mean concentration levels of Fe in the treated water during dry and wet season was 0.12 ± 0.02 mg/L and 0.39 ± 0.12 mg/L respectively, showing iron levels in treated water during the wet season being slightly above the recommended maximum concentration of 0.30 mg/L. According to WHO, iron is an essential trace element in human nutrition and an allocation of 10% of the provisional maximum tolerable daily intake applies to iron from all sources such green vegetables as well as drinking water.

The mean concentration of manganese in Thika reservoir were found to be above the recommended maximum concentration level of 0.10 mg/L during both dry and wet seasons .i.e. 0.17 ± 0.01 mg/L and 0.16 ± 0.04 mg/L respectively. Chania River dry and wet season mean manganese concentration was 0.06 ± 0.01 mg/L and 0.20 ± 0.03 mg/L respectively showing elevation above recommended level during the wet season only. However the mean concentration of manganese in treated water during dry and wet seasons was 0.04 ± 0.01 mg/L and 0.03 ± 0.01 mg/L respectively, which was within the recommended standard.

Mean lead concentration levels in Thika reservoir during the wet season was found to be 0.04 ± 0.01 mg/L which was above 0.01 mg/L recommended by WHO. Lead is likely to be accumulating in Thika reservoir emanating from Thika River which is the reservoir's main feeder river which recorded a mean lead level of 0.02 ± 0.001 mg/L during the wet season.

The mean concentration of Chromium in the catchment was found to be below the WHO guide value of 0.02 mg/L during the dry and wet seasons except in Thika river sampling point where the mean concentration level of 0.045 ± 0.001 mg/L recorded during the wet season (NEMA allowable maximum for chromium level is 0.05 mg/L).

The mean concentration of Nickel in Thika reservoir was found to be 0.024 ± 0.01 mg/L during the wet season, which is slightly above the recommended WHO concentration level

of 0.02 mg/L. These result indicate that there is a likelihood that nickel, which is normally a constituents of inks, dyes and paints could be accumulating in Thika reservoir.

The main sources of chemical pollutants in Chania catchment are small townships and agricultural farms within the catchment that generate waste. Domestic waste such as farmland manure and inorganic fertilizers finally finds its way into water bodies through surface run-off. The townships located in the catchment have petrol stations and small garages that do paint works, car battery repairs and generate waste that is the likely source of heavy metal pollutants such as lead, nickel chromium and Zinc. Other likely sources include natural geophysical processes like weathering of rocks. Anthropogenic activities like riparian cultivation of horticultural crops, Livestock keeping, poultry keeping, tea plantations, roads construction and masonry rock quarrying are also contributors of pollution and degradation of the catchment.

From the findings, the concentration of the metal pollutant iron was not sufficiently removed to recommended WHO standards after treatment and thus the water treatment method was not effective in removal iron.

5.2 RECOMMENDATIONS

Based on the findings of this study, the following is recommended;

- i. As an adaptive measure, the conventional water treatment method can be improved by introducing chemical oxidation technology as a pre-treatment .e.g. use of chemical oxidants such Chlorine dioxide, potassium permanganate, chlorine or by artificial aeration to lower concentration of inorganic pollutants iron and manganese to acceptable levels. Enhancing oxidation will assist convert the dissolved forms of these metals to particulates so that they are removed through the normal sedimentation and filtration processes. However, care should be taken especially when raw water exhibits high turbidity due to likelihood of natural organic matter (NOM), normally a precursor material for the formation of halogenated disinfection by-products (DBPs) impacting

the water. In such scenario, it would limit the use of chemical oxidants such as chlorine and require monitoring of DPBs.

- ii. Creation of awareness and guidance on feasible pollution prevention strategies to help communities living within Chania catchment to stop activities leading to pollution of the environment e.g. Adoption of organic farming instead of use of inorganic fertilizers, domestic waste disposal strategies, soil conservation methods and appropriate handling of garage wastes in environmentally sound ways such as being able to realize hazardous waste streams from their operations and reduce spills. It is recommended among other things that there should be proper monitoring of effluents into receiving water as an integral part of water management in the catchment to enable verification of whether or not imposed standards and regulations are met.
- iii. There should be a comprehensive waste management plan for Chania catchment on waste disposal and education on the dangers of drinking polluted water. The County Government under whom water supply and sanitation lies should design sanitation programmes and propagate these through environmental education throughout the community to prevent pollution of water bodies and the likely spread of water related diseases.

Sufficient information is key for assessing the safety of a drinking-water source and water pollution potential. This assessment requires a variety of information, relating to the hydrogeology, socioeconomic conditions and the range of anthropogenic activities present in the catchment which potentially release pollutants. Further research is therefore recommended to establish such an information inventory as a tool for developing a sound understanding of potential pollution sources and the likelihood with which pollutants may reach the Chania catchment in concentrations that are hazardous to human health.

REFERENCES

- Amirtharajah, A., & Mills, K. M. (1982). Rapid-mix design for mechanisms of alum coagulation. *Journal AWWA*, 74(4), 210-216.
- American Public Health Association (APHA). (2005). *Standard Methods for the Examination of Water and Wastewater* (21st ed.). Washington, D. C: APHA
- Avcievala, S. (1991). *The nature of water pollution in developing countries. Natural Resources* New York: United Nations.
- AWWA. (2000). *Operational Control of Coagulation and Filtration Process*. AWWA Manual (1st ed.). Denver: AWWA
- Bartram, J., Lewis K., R., L., & Wright, A. (2005). Focusing on improved water and sanitation for health. *Lancet Medical Journal*, 365(9), 810–812.
- Beard, J. D., Umbach, D. M., Hoppin, J. A., Richards, M., Alavanja, M. C., Blair, A., & Kamel, F. (2014). Pesticide Exposure and Depression among Male Private Pesticide Applicators in the Agricultural Health Study. *Environmental Health Perspectives*, 122(9), 985.
- Bessell, M. S. (1999). Spectrophotometry: Revised standards and techniques. *Publications of the Astronomical Society of the Pacific*, 111(765), 1426.
- Smethurst, G. (1988). *Basic water treatment for application world-wide*. (1st ed.) London: Thomas Telford.
- Brettar, I., & Höfle, M. G. (1992). Influence of ecosystematic factors on survival of *Escherichia coli* after large-scale release into lake water mesocosms. *Applied and Environmental Microbiology*, 58(7), 2201 – 2210. Washington, D.C: Scientific Society Publisher Allianace
- De Oliveira, A. P., Villa, R. D., Antunes, K. C., & Silva, E. C. (2009). Determination of sodium in biodiesel by flame atomic emission spectrometry using dry decomposition for the sample preparation. *Fuel*, 88(4), 764-766.
- Ecobichon, D. J. (1996). Toxic Effects of Pesticides (in) Casarett & Doull's Toxicology: *The Basic Science of Poisons*, (643-689). New York: McGraw-Hill

- EPA. (1999). Importance of turbidity - Chapter 7. EPA, *Guidance Manual Turbidity Provisions.(7-1)*, Washington, D.C: United States Environmental Protection Agency. Retrieved from http://water.epa.gov/lawsregs/rulesregs/sdwa/mdbp/upload/2001_01_12_mdbp_turbidity_chap_09.pdf.
- EPA. (2002). *Water Treatment Manuals. Coagulation, Flocculation & Clarification.(1st ed.)* Wexford: Environmental Protection Agency (EPA), Ireland. Retrieved from www.epa.ie.
- EPA. (2011). White Paper on Algal Toxin Treatment. *American Water Works Association (AWWA).Ohio Section Technology Committee*. Retrieved from www.ohioalgaefinfo.com.
- EPA. (2012). Cyanobacteria and Cyanotoxins: Information for Drinking Water Systems. EPA-810F11001.Retrieved from: https://www.epa.gov/sites/production/files/2014-08/documents/cyanobacteria_factsheet.pdf.
- FAO. (1993). Control of water pollution from agriculture - FAO irrigation and drainage paper.55(34). Rome: *Food and Agriculture Organization of the United Nations Conference*. Retrieved from <http://www.fao.org/docrep/w2598e/w2598e04.htm>.
- Gebbie, P. (2006). An operator's guide to water treatment coagulants. In *31st Annual QLD Water Industry Workshop-Operations Skills.(15-16)*. England: University Central Queensland. Retrieved from wioa.org.au/conference_papers/06_qld/documents/pdf.
- Geertsema, R., L., W., & Kaufman, J. (2009). *Baseline Review of the Upper Tana Catchment Kenya, Green Water Credits Report 8. ISRIC - World Soil Information, Wageningen*. Retrieved from <http://ww/isric.org> website.
- Gleick, P. H. (2000). A look at twenty-first century water resources development. *Water international*, 25(1), 127-138.
- Government of Kenya, (2006). Kenya Gazette Supplement No. 68: The Environmental Management and Coordination (Water Quality) Regulations, 2006, 5- 9.

- Government of Kenya, (2016). Kenya Gazette supplement No.164: The Water Act (No. 43 of 2016), *The Water Resources Management Rules*, 2007. Legal Notice No.171.
- Government of Kenya, (1986). The Public Health Act (No.242), Revised Edition 2012 [1986].
- Howell, J. M., Coyne, M. S., & Cornelius, P. L. (1996). Effect of sediment particle size and temperature on fecal bacteria mortality rates and the fecal coliform/fecal streptococci ratio. *Journal of Environmental Quality*, 25(6), 1216-1220.
- Hudak, M. E., Dietz, K. J., & Russell, F. (2013). *Estimating Potential Costs of Watershed Development on Drinking Water Treatment (Water Quality modeling Study Report for South Central Connecticut Regional Water Authority)*. Retrieved from www.potomacdwsp.org/wp-content/uploads/2015/03/EstPotentialCostsWatershedDevelopmentCT.pdf.
- Jawson, M. D., Elliott, L. F., Saxton, K. E., & Fortier, D. H. (1982). The Effect of Cattle Grazing on Indicator Bacteria in Runoff From a Pacific Northwest Watershed 1. *Journal of Environmental Quality*, 11(4), 621-627.
- Jeyaratnam J., 1990. Acute pesticide poisoning: a major global health problem. *World Health Statistics Quarterly*, 43 (3): 139-44.
- KEBS. (2007). KS 459 – 1: 2007 Drinking Water - Specification; Part 1: The requirements for drinking Water, (3rd ed.).
- Klockenkämper, R. (2015). *Total-Reflection X-Ray Fluorescence Analysis* (1st ed.). New Jersey: John Wiley & Sons Sons.
- KNDR. (2006). *Kenya National Water Development Report (Case Study Prepared for the 2nd UN World Water Development Report)*. Retrieved from <http://www.eacc.go.ke/docs/Water-Study.pdf>

- Leenherr, J. A. (1981). Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewater. *Environ. Sci. Tech.* (15): 578-587.
- Letterman, R. D., Amirtharajah, A., & O'Melia, C. R. (1999). Coagulation and Flocculation in Water Quality and Treatment. Chapter 6. *R.D. Letterman. McGraw-Hills, New York*.5.
- Letterman, R. D., Amirtharajah, A., & O'melia, C. R. (1999). Coagulation and flocculation in water quality and treatment. *A Handbook of Community Water Supplies*. New York: McGraw-Hills.
- Loucks, D. P. (2000). Sustainable Water Resources Management. *Water International* (25): 3-10.
- Love, P. (1999). Water worries. *Organisation for Economic Cooperation and Development. The OECD Observer*, (217/218), 41. Water worries. Retrieved from <http://www.oecd.org> website.
- Martin, M. B., Simon, M. O., & Mathew, K. K. (2013). Sustainable Catchment Management: Assessment of Sedimentation of Masinga Reservoir and its Implication on the Dam's Hydropower Generation Capacity. *International Journal of Humanities and Social Science*, 3(9), 12.
- Marvin, M.A., & Vallee B. L. (1956). Instrumentation and Principles of Flame Spectrometry Automatic Background Correction for Multichannel Flame Spectrometer. *Analytical Chemistry*, 28 (7): 1066-1067.
- McGrath, S. P., Zhao, F. J., & Lombi, E. (2001). Plant and rhizosphere process involved in phytoremediation of metal-contaminated soils. *Plant Soil*. 2001, 232(12): 207–214.
- Michael, F. C. (2006). Waterborne outbreaks reported in the United States. *Journal of Water and Health* 4(2): 19–30.
- Michael, M. L. (1980). Lead Toxicity and Heme Biosynthesis. *Annals of clinical and laboratory science*. 10(5): 402 - 410

- Mogaka, H., Gichere, S., Davis, R., & Hirji, R. (2005). *Climate variability and water resources degradation in Kenya: improving water resources development and management*. The World Bank.
- Mutua, B. M., & Klik, A. (2007). Predicting daily stream-flow in un-gauged rural catchments- the case of Masinga catchment, Kenya. *Hydrological Sciences*, 52(2), 292-304.
- Napacho, Z., & Manyele, S. (2010). Quality assessment of drinking water in Temeke District: Characterization of chemical parameters. *African Journal of Environmental Science and Technology* 4(11), 775-789. Retrieved Retrieved June 16, 2014, from <http://www.academicjournals.org/AJEST> website.
- NCWSC. (2014). *Nairobi City Water and Sewerage Company Limited Strategic Plan 2014/15- 2018/19*. Kampala Road Ind. Area, Nairobi, Kenya.
- Ongley, E. D. (1996). Control of Water Pollution from Agriculture. *Food and Agriculture Organization of the United Nations Irrigation and drainage Conference paper No.55 (11 -12)*.Rome: FAO.
- Oyhakilome. G., Aiyesanmi, A., & Akharaiyi, F. (2012). Water Quality Assessment of the Owena Multi-Purpose Dam, Ondo State, Southwestern Nigeria. *Journal of Environmental Protection*, (3), 14-25. Retrieved from (<http://www.SciRP.org/journal/jep>) website.
- PAI. (1997). *Sustaining Water, Easing Scarcity: A Second Update. Revised data for the population action international (Report No.97)*. Retrieved from <http://www.populationaction.org/resources/publications/water/> website.
- Pernitsky, D. J., & Edzwald, J. K. (2006). Selection of alum and polyaluminium coagulants: principles and applications. *Research and Technology - AQUA*, 55(2): 121-141
- Perkin, E. (2009). *Atomic spectroscopy - A guide to selecting the appropriate technique and system*. (1st ed.,ebook) MA, USA: PerkinElmer Inc.

- Retrieved from [http://las.perkinelmer.com/content/relatedmaterials /brochures/ bro_ atomicspectroscopytechniqueguide.pdf](http://las.perkinelmer.com/content/relatedmaterials/brochures/bro_atomicspectroscopytechniqueguide.pdf).
- Prabhakar, M., & Mark, D. (2002). *Ultraviolet Spectroscopy and UV Lasers* (Vol.30). New York: Marcel Dekker, Inc.
- Reynolds, T. D., & Richards, P. A. (1996). *Unit operations and processes in environmental engineering* (Vol. 20). Boston, MA: PWS Publishing Company.
- Robert, H. F. (2012). *Essentials of Environmental Health*.(6th ed.) Sudbury, MA : Jones & Bartlett Learning.
- Saenyi, W. W. (2002). *Sediment Management in Masinga Reservoir Kenya* (Doctoral Dissertation, BOKU University of Agricultural Sciences - Viena, Austria). Retrieved from <https://iwhw.boku.ac.at/dissertationen/saenyi.pdf>
- Sagardoy, J. A. (1993). An overview of pollution of water by agriculture. *Water Reports* (19-26) Santiago:FAO.
- Strom, P. F. (2006). Introduction to phosphorus removal. *Wastewater Treatment Operator's Workshop, 91st Annual Conference* (21 -12). Atlantic City, NJ: Rutgers. Edu. Retrieved from : [http://www. water. rutgers. edu/Projects/trading/p-trt-lit-rev](http://www.water.rutgers.edu/Projects/trading/p-trt-lit-rev)
- Sunil, K., Kristen, A., Bhavana, K., Milton, S., & D., T. (2009). *Strategies for Controlling and Mitigating Algal Growth within water Treatment plants*. Denver: Water Research Foundation.
- Tchobanoglous, G., F, Burton., & Stensel, H., D. (2003). *Wastewater Engineering:Treatment, Disposal, and Reuse* (4th ed.).New York:McGraw-Hill
- Tebutt, T. H. (1983). *Principles of Water Quality Control*(3rd ed.). London: Pegamon Press.
- TNC. (2015). Upper Tana – Nairobi Water Fund Business Case. *The Nature Conservancy: Nairobi, Kenya*.
- UNCED. (1992). Protection of the Quality and Supply of Freshwater Resources: Application of Integrated Approaches to the Development, Management and Use

- of Water Resources. *The United Nations Conference on Environment and Development*. 18(21). Rio de Janeiro: UNCED
- UNEP. (2002). Vital Water Graphics - An Overview of the State of the World's Fresh and Marine Waters. Retrieved from https://wedocs.unep.org/bitstream/handle/20.500/Vital_water_graphics.pdf.
- US EPA. (1985). Test methods for Escherichia coli and enterococci in water by the membrane filter procedure (Method #1103.1). *Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH*.
- Vashney, C. K. (2008). Water pollution and management (2nd ed.). Bangalore: *New Age International Limited Publishers*. 2(2),36-89.
- Vivian, B. J., Jeannie, L. D., S., C., & G., C. (2012). *Addressing Nitrate in California's Drinking Water with a Focus on Tulare Lake Basin and Salinas Valley Groundwater* (Report for the State Water Resources Control Board to the Legislature. Center for Watershed Sciences, University of California). Retrieved from <http://groundwaternitrate.ucdavis.edu> website.
- WHO. (1993). *Guidelines for Drinking-Water Quality, Recommendations*. Geneva: World Health Organization.
- WHO. (1996). *Guideline for Drinking-Water Quality. Health Criteria and Other Supporting Information. Background document for development of WHO Guidelines for Drinking-water Quality*. Geneva: World Health Organization
- WHO. (2008). *Guideline for drinking water Quality, Recommendations*. Geneva: World Health Organization.
- WHO. (2011). *World Health Organization - Guidelines for Drinking water quality*. Geneva: World Health Organization
- Wilschut, L. (2010). Land use in the Upper Tana. Technical report of a remote sensing based land use map. *Green Water Credits*.(Report No. 9 ISRIC).. Wageningen,Netherlands: ISRIC - World Soil Information. Retrieved from <https://www.cabdirect.org/cabdirect/abstract/20103308401>

- Zakir, H. M., Kohinoor, B., Mohiuddin, K. M., & Arafat, M. Y. (2011). Quality Assessment of Waters of Bogra City area, Bangladesh. *Journal of Agroforestry and Environment*, 3(2), 21 – 25.
- Xiaowei, G. (1991). Atomic Absorption, Atomic Fluorescence Spectrometry and Flame Emission Spectrometry [J]. *Chinese Journal of Analysis Laboratory*, 7(6), 10-24

APPENDICES:

Appendix I: Table of Values of Water Quality Parameters Analysed (dry & wet season)

Table of Mean values, Standard Deviations of water parameters analysed (\pm S.D; n=18 , Maximum - Minimum)												
Water Quality Variable	Desired limit	Season	A		B		C		D		E	
			X \pm S.D	Range	X \pm S.D	Range	X \pm S.D	Range	X \pm S.D	Range	X \pm S.D	Range
Turbidity (NTU)	5 NTU	Dry season	7.04 \pm 0.39	6.20 - 7.70	1.50 \pm 0.05	1.45 - 1.60	3.00 \pm 0.15	2.84 - 3.29	5.20 \pm 0.69	4.09 - 6.67	0.40 \pm 0.13	0.33 - 0.70
		Wet Season	107.89 \pm 5.85	65.00 - 181.00	6.93 \pm 0.26	6.50 - 7.20	38.09 \pm 5.08	33.00 - 45.50	96.0 \pm 45.62	54.00 - 169.00	1.30 \pm 0.42	0.80 - 2.17
TDS (mg/L)	500 mg/L	Dry season	17.66 \pm 0.58	17.10 - 19.00	11.91 \pm 0.53	11.26 - 13.00	34.52 \pm 1.15	32.00 - 36.04	29.30 \pm 2.60	27.20 - 34.00	42.77 \pm 6.17	38.06 - 55.00
		Wet Season	35.40 \pm 0.96	34.20 - 37.10	12.30 \pm 0.34	11.80 - 12.70	10.90 \pm 0.37	10.70 - 11.80	33.20 \pm 0.60	32.50 - 34.20	65.50 \pm 2.40	64.0 - 71.0
pH Value	6.5-8.5	Dry season	7.10 \pm 0.10	6.90 - 7.23	6.80 \pm 0.03	6.75 - 6.85	7.10 \pm 0.22	6.60 - 7.33	7.00 \pm 0.04	6.90 - 7.00	7.30 \pm 0.15	7.01 - 7.40

		Wet Season	6.70±0.05	6.71 - 6.80	6.81±0.02	6.75 - 6.79	6.60±0.03	6.57 - 6.66	6.90±0.05	6.85 - 6.98	7.30±0.16	7.10 - 7.50
EC (µS/cm)	600 µs/cm	Dry season	27.30±1.60	26.00 - 31.00	16.90±0.25	16.60 - 17.50	53.10±2.65	50.90 - 58.00	40.60±1.22	38.00 - 42.00	68.70±5.83	61.00 - 80.00
		Wet Season	52.32±1.15	51.10 - 54.10	18.77±0.29	18.40 - 19.20	16.64±0.40	16.20 - 17.30	48.94±0.62	47.80 - 49.50	91.81±3.35	86.00 - 95.00
Temp. (°C)	°C	Dry season	20.0±0.10	19.8 - 20.1	20.0±0.09	19.8 - 20.1	19.0±0.05	19.0 - 19.1	18.9±0.30	18.5 - 19.5	20.7±0.25	20.5 - 21.0
		Wet Season	18.9±0.17	18.7 - 19.1	19.6±0.37	19.0 - 20.0	18.1±0.21	18.0 - 18.5	18.3±0.35	18.0 - 18.5	19.4±0.31	19.0 - 20.0
MPN per 100 ml	Nil	Dry season	1067±153	-	333±115	-	1233±152	-	667±153	-	0	-
		Wet Season	1900±625	-	667±153	-	767±306	-	1367±306	-	0	-
Mean Sodium conc. (mg/L)	300 mg/L	Dry season	4.14±0.05	4.09 - 4.20	0.86±0.03	0.84 - 0.89	0.93±0.00	0.92 - 0.93	3.86±0.02	3.84 - 3.87	9.34±0.02	9.32 - 9.37
		Wet Season	4.61±0.36	4.31 - 5.00	0.80±0.02	0.78 - 0.82	0.97±0.01	0.96 - 0.98	4.16±0.29	3.98 - 4.50	9.72±0.06	9.69 - 9.78

Mean Aluminium conc. (mg/L)	0.10 mg/L	Dry season	0.03±0.01	0.02 - 0.04	0.04±0.01	0.02 - 0.06	0.02±0.01	0.02 - 0.03	0.04±0.02	0.02 - 0.06	0.08±0.01	0.07 - 0.10
		Wet Season	0.03±0.01	0.02 - 0.05	0.04±0.01	0.03 - 0.05	0.02±0.01	0.01 - 0.04	0.03±0.01	0.02 - 0.05	0.09±0.01	0.08 - 0.11
Mean Nitrates concentration (mg/L)	10.0 mg/L	Dry season	4.23±0.21	4.01 - 4.44	4.29±0.31	3.98 - 4.60	4.25±0.11	4.14 - 4.36	3.33±0.50	2.83 - 3.83	3.29±0.24	3.05 - 3.53
		Wet Season	6.29±0.52	5.76 - 6.81	6.83±0.60	6.23 - 7.43	6.65±0.40	6.25 - 7.05	6.59±0.30	6.29 - 6.89	6.38±0.61	5.77-6.99
Mean Phosphate concentration (mg/L)	mg/L	Dry season	6.03±0.47	5.50 - 6.51	3.29±0.45	2.83 - 3.74	3.12±0.63	2.10 - 3.76	3.45±0.45	3.01 - 3.91	3.34±0.11	3.23 - 3.43
		Wet Season	6.98±0.68	6.31 - 7.67	3.64±0.59	3.03 - 4.23	2.17±0.11	2.07 - 2.28	5.94±0.27	5.68 - 6.22	3.46±0.77	2.59 - 4.23
Mean Chloride Value (mg/L)	250 mg/L	Dry season	2.83±0.31	2.44 - 3.22	2.67±0.36	2.23 - 3.11	4.41±0.61	3.51 - 5.13	3.96±0.15	3.77 - 5.12	10.15±1.38	8.02 - 12.03
		Wet Season	5.11±0.72	3.89 - 5.45	3.38±0.33	2.94 - 3.76	4.47±0.48	3.86 - 4.95	4.85±0.35	4.24 - 5.12	12.24±1.87	9.73 - 15.07

Appendix II: Table of Heavy Metal Concentrations (mg/L) (dry & wet season)

Dry season (Mean ± S.D; n=6)									
Sampling Point	Mn	Fe	Cu	Pb	Zn	Cr	Ni	Ca	K
A-Chania River	0.06±0.01	1.35±0.01	< 0.01	< 0.01	< 0.01	< 0.02	< 0.02	2.96±0.16	2.08±0.14
B-Reservoir Discharge	0.17±0.01	0.26±0.09	< 0.01	< 0.01	< 0.01	< 0.02	< 0.02	0.91±0.22	0.22±0.02
C-Thika River	0.04±0.00	0.26±0.07	0.01±0.00	< 0.01	< 0.01	<0.02	<0.02	1.08±0.29	0.31±0.05
D-Inflow to Plant	0.07±0.00	0.75±0.07	< 0.01	< 0.01	0.058±0.01	< 0.02	< 0.02	2.95±0.01	0.71±0.05
E-Treated Water	0.04±0.01	0.12±0.02	< 0.01	< 0.01	0.032±0.00	<0.02	<0.02	3.55±0.50	0.57±0.04
Wet season (Mean ± S.D; n=6)									
A-Chania River	0.20±0.03	3.78±0.17	< 0.011	< 0.01	0.02±0.00	< 0.015	< 0.02	1.41±0.60	1.10±0.54
B-Reservoir Discharge	0.16±0.04	0.36±0.08	< 0.01	0.04±0.01	< 0.01	< 0.02	0.02±0.01	0.89±0.06	0.41±0.08
C-Thika River	0.09±0.05	1.16±0.17	0.02±0.00	0.02±0.00	0.04±0.02	0.05±0.00	< 0.02	0.89±0.58	0.22±0.17
D-Inflow to Plant	0.09±.01	2.26±0.27	0.01±0.00	0.01±0.00	0.02±0.00	< 0.02	< 0.02	1.74±0.40	0.86±0.27
E-Treated Water	0.03±0.01	0.39±0.12	0.011±0.00	0.01±0.00	0.02±0.00	< 0.017	< 0.02	2.43±0.93	1.03±0.58
STD	0.1	0.3	0.05	0.01	1.5	0.05	0.02	250	-

Appendix III: Tables (a) & (b) - Dry and wet seasons MPN of coliforms

Table (a): Number of Tubes giving Positive Reaction out of 5 during dry Season (Most probable number (MPN) of coliforms per 100 ml of sample and 95% confidence limit for (five 10-ml, five 1-ml and five 0.1-ml test portions - by Mc Crady's table)							
Source of water	Sample No.	Sampling point	No. of tubes giving a positive reaction:			MPN (per 100 ml of 100 times diluted water sample)	MPN of coliform organisms in 100 ml of the original water
			5 of 10ml	5 of 1ml	5 of 0.1ml		
Chania river	1	A1	2	1	1	9	900
	2	A2	2	3	0	12	1200
	3	A3	3	0	1	11	1100
Thika Reservoir discharge	4	B1	1	0	1	4	400
	5	B2	0	1	0	2	200
	6	B3	0	2	0	4	400
Thika river	7	C1	3	1	0	11	1100
	8	C2	3	1	1	14	1400
	9	C3	2	3	0	12	1200
Inflow to water Woks	10	D1	2	0	1	7	700
	11	D2	3	0	0	8	800
	12	D3	2	0	0	9	500

Clear well	13	E1	0	0	0	0	0
	14	E2	0	0	0	0	0
	15	E3	0	0	0	0	0

Table (b): Number of Tubes giving Positive Reaction out of 5 during wet Season (Most probable number (MPN) of coliforms per 100 ml of sample and 95% confidence limit for (five 10-ml, five 1-ml and five 0.1-ml test portions - by Mc Crady's table)

Sampling Point	Sample No.	Sampling point	No. of tubes giving a positive reaction:			MPN (per 100 ml of 100 times diluted water sample)	MPN of coliform organisms in 100 ml of the original water
			5 of 10ml	5 of 1ml	5 of 0.1ml		
Chania River	1	A1	4	2	1	26	2600
	2	A2	3	2	1	17	1700
	3	A3	3	2	0	14	1400
Thika Reservoir discharge	4	B1	2	0	0	5	500
	5	B2	3	0	0	8	800
	6	B3	2	0	1	7	700
Thika river	7	C1	2	0	0	5	500
	8	C2	2	1	0	7	700

	9	C3	3	1	0	11	1100
Inflow to water Woks	10	D1	4	1	0	17	1700
	11	D2	3	1	0	11	1100
	12	D3	4	0	0	13	1300
Clear well	13	E1	0	0	0	0	0
	14	E2	0	0	0	0	0
	15	E3	0	0	0	0	0

Appendix 4: Procedure for Presumptive Test for Microbiological Analysis

Materials required; 3 Durham tubes of double strength lactose broth (DSLБ), 6 Durham tubes of single strength lactose broth (SSLB), 1 10ML pipette, 1 1ml pipette, Lactose Broth, Disposable petri dishes, Universal bottles, Nutrient agar and Eosin Methane blue agar.

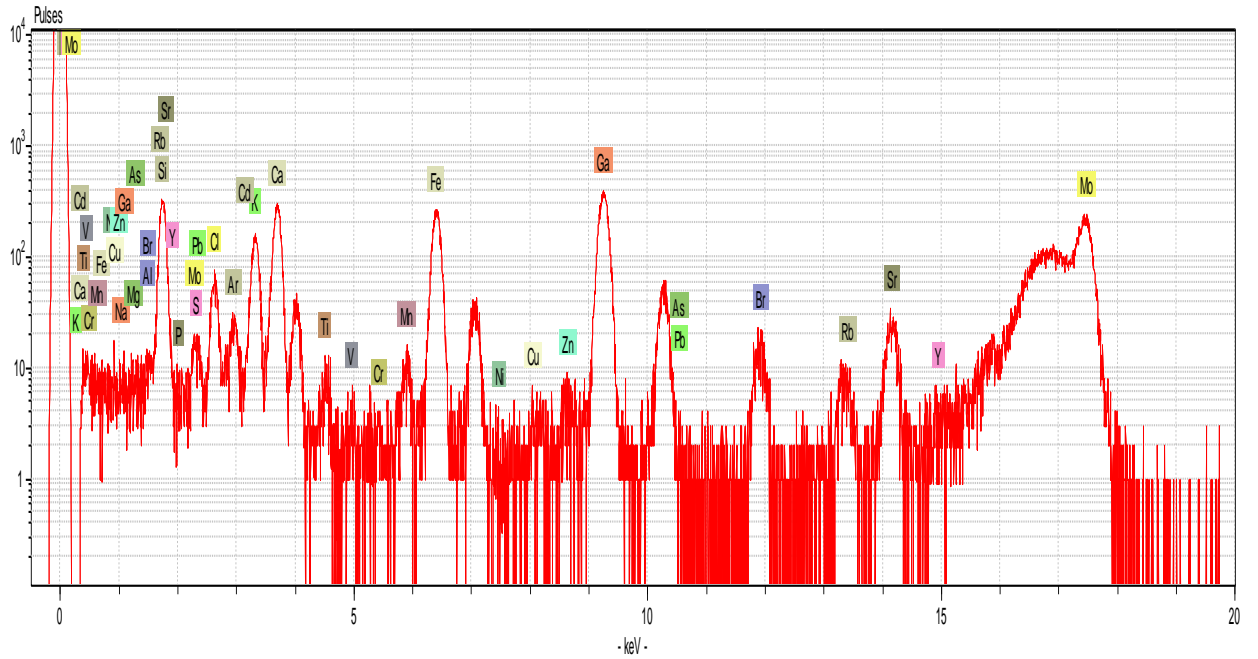
Procedure;

- i. All apparatus were sterilized.
- ii. MacConkey Broth (medium) was prepared in Double Strength and Single Strength.

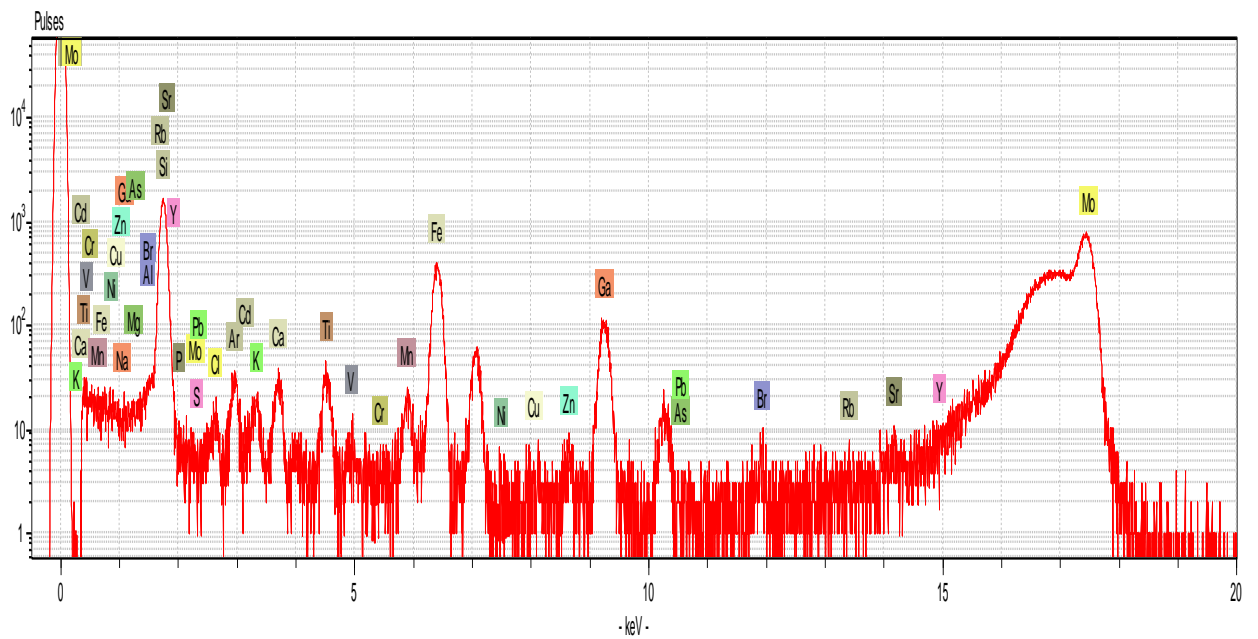
The double strength MacConkey Broth was prepared by dissolving 70g/L of the powder in 1.0litre of distilled water while single strength was prepared by dissolving 35g/L in 1.0 L of distilled water.
- iii. The medium was sterilized at 121°C in an autoclave machine.
- iv. Three sets of three universal bottles were prepared. One set was DSLB and two sets were SSLB.
- v. Each bottle was filled with 10mls of the medium.
- vi. The bottles were labeled according to the amount of sampled water that was to be dispensed in each. (10ml, 1ml and 0.1 ml) respectively.
- vii. The water samples were shaken to ensure even distribution of micro-organisms.
- viii. With a 10ml pipette, 10mls of water were transferred to each of the DSLB.
- ix. With a 1.0ml pipette, 1.0ml of water were transferred to each of the three bottles of SSLB.
- x. 0.1mls were transferred to each of the last three bottles of SSLB.
- xi. The bottles were then incubated for 24hrs at 37°C.
- xii. After 24 hours, the bottles were checked and results recorded.

Appendix V: Sample TXRF Spectra for Heavy Metal Analysis (Chania River)

a) Dry Season (Chania River)



b) Wet Season (Chania River)



Appendix VI: Free Residual Chlorine in treated water (mg/L)

Sampling Point	Dry Season		Wet Season	
	X±S.D	Range	X±S.D	Range
E-Treated Water	1.15±0.12	1.00 - 1.30	1.27±0.10	1.10 - 1.40

Appendix VII: Heavy Metal Analysis procedure by Total X-ray Fluorescence

Methodology for elemental content determination in liquid samples by Total X-ray Fluorescence (TXRF) technique (using S2 PICOFOX Spectrometer).

River Water samples were analysed for heavy metals using TXRF technique as follows;

A) Sample preparation for TXRF analysis

- i. Aliquots of 20 ml of each sample were measured into clean vials.
- ii. Amounts of 10µL of 1000ppm Gallium stock solution were added into each sample (as internal standard) resulting into a concentration of 0.5ppm Ga per sample.
- iii. Each sample was homogenized by mixing using a vortex mixer for one minute.
- iv. Aliquots of 10µL of each sample were pipetted onto clean quartz carrier using a micro-pipette.
- v. The carriers were then dried in an oven at temperature of 60°C.

B) Sample spectrum acquisition and quantitative analysis

- a. Each sample carrier was irradiated for 1000 seconds using a S2 PICOFOX TXRF Spectrometer which was operated at 50kV and a current of 1000µA. The spectrometer uses a molybdenum anode.

- b. Evaluation of the measured spectra was done using S2 PICOFOX software on the basis of the chosen elements.
- c. The concentrations were calculated based on the net intensities of the analyte peak elements and that of the Internal standard as per the following formula;

$$C_x = \frac{N_x / S_x}{N_{is} / S_{is}} \times C_{is} \dots\dots\dots \text{equation 1}$$

Where,

- C_x ----- Concentration of the analyte
- C_{is} ---- Concentration of the internal standard
- N_x ----- Net intensity of the analyte
- N_{is} ----- Net intensity of the internal standard
- S_x ----- Relative sensitivity of analyte
- S_{is} ----- Relative sensitivity of internal standard

- d. Quantitative results obtained were copied to an excel worksheet (as is the protocol of the software). The worksheet was named Raw Data.
- C) Data treatment in excel
- a. All the data in Raw data worksheet was copied to Calculated worksheet where unnecessary data columns like Line, Energy/Kev, Cycl., Net. Background Sigma and Chi were deleted. Also, unnecessary element row lines such as those of Si, Ar, As-L1, Se-L1, etc were removed.
 - b. Data in Calculated worksheet were further evaluated for averages and standard deviations for each set of sub-samples. AVERAGE and STDV functions in excel were used.
 - c. Residual data in step (b) was copied to Final worksheet. To these data, all unnecessary columns (i.e. X1, X2 & X3 for sample) were deleted leaving the

calculated averages (Avg.Conc.,Avg.SigmaC) and standard deviations (Stdev) values as the final concentrations data.

Appendix VIII: Procedure for determination of Phosphate using spectrophotometry method

Involves conversion of phosphate to molybdenum blue whose colour is monitored spectrophotometrically at 660nm.

Reagents required.

1. Ammonium molybdate (0.005M). Dissolve 6.1793g of ammonium heptamolybdate in 0.4M nitric acid.
2. Ascorbic acid (0.7% w/w). Dissolve 7.0000g of ascorbic acid in 10ml of water and add 10ml of glycerine.
3. Phosphate stock solution 10mg/L. Dissolve 0.439g of potassium dihydrogen phosphate in 10ml of water.

Dilute the above phosphate stock solution with distilled water to prepare standard solutions with containing 0, 0.5, 1, 1.5, 2, 2.5, 3 mg/ml phosphorous as phosphate.

Colour formation and measurement;

Add 3ml of molybdate to 3.0 ml of ascorbic acid solution in a 50 ml volumetric flask. Shake to mix and add 10 ml of sample. Add distilled water to the mark. Mix well and allow to stand 10 – 15 minutes. Then measure the absorbance at 660mm.

Use method to find the amount of phosphate in the water samples.

- i. Measure the absorbance of each standard and samples at least three times, in order of increasing concentration followed by that of sample solutions and calculate the mean absorbance for each.
- ii. Plot a graph of mean absorbance vs corresponding phosphorous concentration and use it to calculate the phosphorous concentration in the samples.

Appendix IX: Procedure for determination of Chloride using Spectrophotometry

The method is based on the formation of the characteristic iron (III) thiocyanate colour, when chloride ion reacts with mercury (II) thiocyanate in the presence of iron (III) ions.

a. Preparation of reagents;

- i. Alcoholic mercury (II) thiocyanate: 0.030g of mercury (II) thiocyanate were dissolved in 100ml of industrial methylated spirit and transferred into a 250ml conical flask. This was warmed gently to dissolve. The resulting solution was stored in a glass stoppered reagent bottle.
- ii. Ferric alum solution: 6.0g of ferric alum were dissolved in 100ml of 6M nitric acid. The solution was stored in a 250ml glass reagent bottle.
- iii. Standard stock solution of chloride ion: 1000ppm Cl^- ion in double deionised water was made up using analytical grade sodium chloride as a source of Cl^- ion.
- iv. Standard solutions for chloride ion were made by dilution of 1000ppm standard stock solution into 100 ppm using double deionised water in 250ml volumetric flask. This was further made into working solutions containing 15, 20, 40, 60 and 80ppm of Cl^- ion respectively using a 50ml volumetric flask.

b. Preparation of reagent blank;

An amount of 10ml double deionised water was added into a clean 100ml beaker. 2.0ml of ferric alum solution and 1.0ml of alcoholic mercury thiocyanate solution were added. After ten minutes the reagent blank was ready for use in reference beam of the spectrophotometer.

c. Determination of absorption spectrum of ion (IIF) thiocyanate;

An amount of 10ml of a 50 ppm solution of Cl^- was added into a 100ml beaker after which 2.0ml of ferric alum and 1.0ml of thiocyanate reagent was added. Using 1cm cell, an absorption spectrum of the iron (III) thiocyanate complex was obtained with the Spectrophotometer set on 0-1.0 Absorbance range, slow scan setting and a wavelength range of 430 – 850nm.

d. Preparation of calibration curve;

An amount of 10 ml for each working standard solutions ranging from 15 – 100 ppm Cl^- was added into separate 100ml beakers. To each solution 2.0ml of ferric alum solution was added followed by 1.0ml of Mercury (II) thiocyanate and then the absorbance of each solution was measured at 470nm using a 1 cm cell, against a reagent blank in the reference beam. A curve was plotted of absorbance against ppm of Cl^- to obtain a calibration curve.

e. Determination of Cl^- in water samples;

This was done by using a 10ml aliquot of water samples and adding the reagents as indicated above and then determining the absorbance of each solution. Using the calibration graph, the concentration of Cl^- in ppm was determined in each water sample.

Appendix X: Procedure for determination of Aluminium using Spectrophotometry

Aluminum was analyzed using VIS spectrophotometer HACH DR 3900 (spectrophotometry method 8012) according procedure described in the Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

In this method samples were digested using mixture 3:1 of nitric acid and hydrochloric for determining total aluminum. All glassware was rinsed with 6.0N HCl and deionized water before use to remove contaminants from the glass. The blank was prepared by tacking 10 ml of the mixture and pouring it into a square sample cell. This was added one bleaching 3 reagent Powder Pillow and timer pressed. The cell was swirled vigorously for 30 seconds. The solution turned into a light red to medium orange color. The timer was pressed again for a 15-minute reaction period. The sample temperature was maintained between 20–25 °C. Aluminum standard solution of 0.4mg/L was prepared and used to make appropriate dilutions of 0.02, 0.04, 0.06, 0.08, 0.1 and 0.12mg/l. A 50ml cylinder was filled with standards and in the same manner the sample water was prepared. These were filled with distilled water to the mark. Then one Ascorbic Acid Powder Pillow was added and closed with a stopper. It was inverted several times to dissolve the Powder. After dissolution one powder pillow of Aluminum reagent (AluVer 3) was added to the solution and then inverted severally for one minute. An orange to orange-red color developed indicating aluminum was present. The analysis was conducted by placing the blank into the cell holder with the fill line facing right. Then 10 ml of solution was taken from the cylinder and poured into a second square sample cell. The results were measured at 522 nm.

Appendix XI: Procedure for Determination of Sodium by Spectroscopy

Determination of Sodium was done by Flame Atomic Emission (FAES, Model AA-6200 Shimadzu) Spectrophotometer as follows;

a) Determination of Cations for sodium (Na^+);

Water sample 100ml, was digested by adding 5.0 ml of perchloric acid and nitric acid in the ratio of 1:3. It was heated without boiling till it evaporated to about 20 to 15 ml, then was filtered using a 0.45 μm filter paper and topped up to 100ml using the distilled water.

b) Preparation of 1000 ppm stock AE standards for sodium;

2.52174g of NaCl (dry) was dissolved in 1000ml volumetric flask using distilled water and transferred into clean sample bottles. Working Standards for sodium 0.1, 0.5, 10, 20, 40, 60, 80, 100 mg/l of the sodium metal were made using appropriate dilutions.

c) Determination of sodium;

Flame photometer was used for analysis of the alkali metallic elements as follows; each of the working standards in the different volumetric flasks was aspirated into the flame, starting with the least concentrated to the highest. The sample was run in the same manner. This was repeated for sodium metal for at least three times and steady reading recorded. The results were used to draw a graph that gave the best line of fit for emission intensity against concentrations. The analysis of Na^+ were typically determined at low temperatures at absorbance obtained at 589 nm.

Appendix XII: Procedure for Determination of Nitrates Spectrophotometry Method.

Determination of Nitrates was done by UV/ Vis Spectrophotometry Method as follows;

- i. Stock solution was prepared from potassium nitrate (Analytical grade) containing 1000 ppm).
- ii. Nitrate standards were prepared from the stock solution in the range of 2.0, 4.0, 6.0, 8.0, 10.0 ppm respectively.
- iii. Measurements were taken at two wavelengths, 210 nm (absorbance due to nitrates) and 275 nm (interference due to dissolved organic matter) and distilled water was used as a reference.
- iv. An aliquot of 30ml water sample under investigation was transferred to 50ml volumetric flask. This was diluted to the mark using distilled water. The absorbance of the sample was measured.
- v. Calculations: For sample and standards, the absorbance at 275 nm was subtracted four times from that at 210 nm.
- vi. A standard curve was prepared for absorbance against the concentration of the standards and the sample concentrations were therefore obtained from the corrected absorbencies.