



UNIVERSITY OF NAIROBI
COLLEGE OF BIOLOGICAL AND PHYSICAL SCIENCES
DEPARTMENT OF CHEMISTRY

ASSESSMENT OF THE WATER QUALITY OF SELECTED BOREHOLES IN
MANDERA TOWN AND ITS ENVIRONS

BY

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DECLARATION

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

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This thesis has been submitted with our approval as University supervisors.

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ABSTRACT

Mandera town and its environs rely on boreholes, piped water, seasonal rivers and rain water for domestic use. Water scarcity and population rise in the county have made people rely more on borehole water. Increased pastoralism has led to increased pollutants that have posed a potential threat to surface and borehole water quality. This in turn poses a potential adverse health effects on the residents.

This study was undertaken to assess the physical and chemical properties; investigate the presence of *E-Coli*; and compare these values with the WHO and NEMA guideline values. The study was carried out between October 2014 and March 2015 and a total of five borehole water samples were collected from five boreholes at different sites in Mandera Town, namely Mandera Town, Elwak, Takaba, Shimbir Fatuma and Banisa. Each of the five borehole samples were analyzed for pH, electrical conductivity, total dissolved solids (TDS), fluoride, chloride, nitrate, ammonium, potassium, sodium, lead, zinc and *E-coli*. The results were as follows : pH (5.1-7.67), electrical conductivity (840-6940 $\mu\text{S}/\text{cm}$), total dissolved solids (520-4302 mg/L), fluoride (0-1 mg/L), chloride (7.99-119.9 mg/L), nitrate (0.316-2.26 mg/L), ammonium (0-0.66 mg/L), potassium (4.7-101.4 mg/L), sodium (11.2-46.4 mg/L), lead (not detected), zinc (0.057-0.189 $\mu\text{g}/\text{L}$) and *E-coli* (nil/100 mL). pH values for all boreholes were within the guidelines except Banisa (5.1), Shimbir Fatuma (5.3) and Mandera Town (5.3) which were lower compared to WHO and NEMA standard (6.5-8.5). Electrical conductivity was within WHO guideline value (2000 $\mu\text{S}/\text{cm}$) except at Elwak (6940 $\mu\text{S}/\text{cm}$). Elwak also had a higher TDS (4302 mg/L) as compared to WHO (1000 mg/L) and NEMA (1200 mg/L). In all the five boreholes, fluoride, chloride, ammonium, nitrate, zinc, lead, and *E-coli* were all below

the WHO and NEMA guideline values. At Banisa, Mandera Town and Takaba only pH did not conform to standards while at Elwak and Takaba all parameters conformed to standards except for electrical conductivity and total dissolved solids. No *E.coli* was detected in all the samples.

DEDICATION

I dedicate this project to my husband Hussein Mohammed, my sons Imran Hussein and Sadaat Hussein, my family and my supervisors Prof. A.O. Yusuf and Mr. G. Wafula.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AAS	Atomic Absorption Spectrometry
EMCA	Environmental Management and Co-ordination Act
mg/L	Milligrams per liter
mL	Milliliters
NEMA	National Environment Management Authority
pH	Hydrogen ion Concentration in Moles / liter
Ppb	Parts per billion
PPM (ppm)	Parts per Million
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
TXRF	Total Reflection X-ray Fluorescence
UNICEF	United Nations Children Fund
UV-VIS	Ultraviolet Visible
WHO	World Health Organization
WSUP	Water and Sanitation for the Urban Poor

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CHAPTER ONE

INTRODUCTION

1.1 Water in Kenya

According to United Nation report of 2010, Kenya has been classified as a country with the most stressed people in the world and with a constant rising poverty index. Kenya has a population of about 40 million people with an annual growth of around 2.6% (WHO/UNICEF, 2010).

Northern Kenya has been known to be an area prone to water scarcity, and year round arid climatic conditions with small percentage of the country's land identified to be best in agriculture. The area has recently faced natural disasters which led to soil degradation together with refugee displacement problems in the eastern part of northern Kenya (UN, 2015).

According to research conducted on water supply and sanitation by the Joint Monitoring Programme (JMP) in the year 2008, about 59% of Kenyans majority from urban areas had access to uncontaminated drinking water with 19% of the urban population having access to piped water (Gleick, 1993). The report also recorded a decrease in access to uncontaminated water sources in the urban areas between the year 1990 and 2008 from 91% and 83%. However, rural areas recorded increased values from 32% to 52% for the same period. Between the year 2006 and 2007, it was reported that approximately 37% of Kenyans were able to access adequate and clean water in their households (WHO/UNICEF, 2010). During the same period, Nairobi city recorded 35% accessibility which was less compared to 46% reported for the year 2005-2006. Tetu

Aberdare water and Sanitation Company recorded the highest value (72%) while Muthambi in Meru South District recorded the least accessibility of 4%) (WHO/UNICEF, 2010).

Poor access to uncontaminated water in the country has been contributed by the natural water resources not providing enough water to most areas. There is also insufficient water basins in the country which has resulted to a large number of people not able to access any fresh water. Most poor urban dwellers have been forced to relocate to slum areas where water and sanitation services are inadequate. Overcrowding in these places leads to deterioration in health conditions.

Political issues influence development in most areas in Kenya where more developed areas receive more resources as opposed to areas occupied by the poor. In the developed world privatization of water supply has led to increased access. On the other hand privatization of the same in poor countries has led to low access due to increased cost which the impoverished cannot afford. This has led to a majority of the people to lack piped water which has contributed to poor sanitary conditions (UNEP, 1990).

Poor access to water resources has led to vulnerable people in the community (women and children) spending much of their time in looking for water which exposes them to serious danger and also makes them susceptible to water borne diseases (WHO/UNICEF, 2010). Rapid exposure to waterborne diseases in Kenya has been attributed to contaminated water which is becoming a big health problem due to water pathogens causing sporadic epidemics such as cholera and parasitic infections.

Research from previous studies gave clear evidence that people living in rural areas like Mandera town find it hard to access quality water for both domestic and

agricultural use. Water quality assessment of the sources of water supplying the town is required so that the data obtained can be used by local authorities to provide quality water to the people. The water sources to be considered are boreholes as this is the main domestic water source accounting for 80% of the total.

1.2 Problem Statement

Water sources in Mandera town and its environs include boreholes, piped water, seasonal rivers and rain water. Due to the rapid rise in population and inadequate rainfall, more people have come to rely on borehole water to satisfy the ever increasing domestic needs.

With rapid expansion of pastoralism around Mandera, considerable quantities of pollutants have posed a potential threat to the water quality of surface and borehole waters which has the potential to cause adverse health effects on the residents. Currently there has not been enough research done to clearly state the quality of water that is consumed domestically in Mandera Town. At concentrations higher than recommended values, fluoride can lead to adverse effects like dental fluorosis. Higher levels of lead, copper and zinc can also lead to serious health effects. Therefore assessment of drinking water quality would provide adequate data to facilitate appropriate mitigation measures to be implemented.

1.3 Objectives

1.3.1 Overall Objective

To characterize the quality of drinking water from five boreholes in Mandera town and its environs.

1.3.2 Specific Objectives

The specific objectives were:

1. To assess the physical properties of some five selected boreholes in Mandera Town and its environs.
2. Investigate the chemical properties of some five selected boreholes in Mandera Town and its environs.
3. To investigate the presence of *E-Coli* in the five borehole waters in Mandera Town and its environs.
4. To compare the determined values with the NEMA and WHO guideline values.

1.4 Justification

Mandera County is characterized by arid and semi-arid climate with pastoralism as the main occupation that requires adequate supply of water to satisfy both human and livestock needs. However, there is lack of comprehensive data on quality of these sources of water. A significant number of residents in Mandera town and its environs have stained teeth which may be an indication of high levels of fluoride ions in water.

This study may create awareness and help key policy agencies responsible for public health, pollution control, food safety and nutrition such as World Health Organization, Kenya Bureau of Standards, and United Nations Environmental Programme (UNEP) in developing strategies to manage the environment and provide quality water to the community.

CHAPTER TWO

LITERATURE REVIEW

2.1 Global water distribution

Water is a very important resource in the Earth. In all its forms water is known to be vital. 70.9% of the Earth's surface is covered with water of which 97% are in the oceans, 2.1% glaciers including Antarctica and Greenland ice caps, 0.87 % ground water and 0.03 % are in surface waters (rivers, lakes, vapor, clouds and precipitation). Approximately 3 % of the planet's water is fresh with ice and ground water comprising of 98.8%. Lakes, rivers form approximately 0.3% (Leopold and Davis, 1996).

2.2 Water Quality Parameters

2.2.1 Total Dissolved Solids (TDS)

Total Dissolved Solids are secondary contaminants which can be defined as a measure of a combined form of inorganic and organic substances dissolved in water. Organic compounds will form ionized or unionized species in solution. Inorganic compounds will be in ionized form. They are considered to be a threat at a concentration above 500 mg/L whereby some water contaminants may lead to adverse health effects. (Davis,1968). Agricultural activities, leaching of contaminated soil, residential runoff, polluted water discharge points from sewage treatment plants and industrial effluents are the main sources of TDS in water bodies. TDS are composed of chemicals from nutrients and storm runoff which may be anions, cations or agglomerations. They include phosphates, nitrates, calcium ions, sodium ions, potassium ions, chloride ions and pesticides arising from surface runoff. Dissolved solids can be caused through weathering

and dissolution of soils and rocks. TDS concentrations vary significantly due to different geological make-up, which led to differences in mineral composition and solubility. WHO recommends a maximum limit of 1000 mg/L in domestic water (Terrio, 1995).

Gravimetric and electrical conductivity methods are the main two methods considered for TDS determination. The more accurate of the two is the gravimetric method, although it is time consuming. It involves evaporation of a known volume of the liquid solvent and the mass of solid residue left is then used in determination of its content. Based on TDS values in mg/L water can be classified as fresh water (less than 1000), brackish (1000-10,000), saline water (10,000-30,000) and brine (greater than 30,000).

2.2.2 Conductivity

Conductivity can be defined as the ability of water to allow electric current to pass through. The conductivity of the ions will be determined by total ion concentration, mobility and valence. Temperature also has an effect on electrical conductivity. Concentration of dissolved ions in water is proportional to electrical conductivity. A correlation of conductivity with TDS measurements indicates that conductivity gives an approximate value of TDS which is normally within an accuracy of 10% (Garret 1994). Some organic compounds like alcohols, oils, sugars and phenols have a low electrical conductivity (Waldron and Willey, 1996).

Water conductivity of ground waters, streams and rivers can be affected by the geology of the region above which the water flows. Rivers which flow through regions whose geology is made up of granite bedrock are expected to have low conductivity.

Granite contains a lot of inert materials which have low solubility in water hence lower conductivity. In addition, streams flowing over regions with clay soils are likely to have higher conductivity because clay soils have materials which ionize when dissolved in water (Heritage and Evans, 1999). Discharges by inefficient sewage system into the stream can also increase conductivity due to the existence of nutrients like phosphates, nitrates and chlorides just to name a few. Conductivity has a direct proportionality to the ions concentration and is measured in mho or Siemens per centimeter (APHA, 1992).

2.2.3 pH

pH can be defined as a measure of negative logarithm of hydrogen ion concentration in moles per liter (M). Uncontaminated water naturally dissociates into ions making a solution of 10^{-7} each of H^+ and OH^- of which the negative logarithm is 7 making the pH of water to be 7. Solutions with H^+ concentrations higher than 10^{-7} leads to water with pH values less than 7 hence considered to be acidic while solutions having ions that are lower than 10^{-7} have pH values higher than 7 and is considered to be basic or alkaline.

pH can be affected by the ionic strength of a solution. This is because water with pH less than 6.5 could be considered corrosive and acidic with possibility of water having metal ions including copper, zinc, lead, iron and manganese. Electrical potential can be affected by pH due to the reaction of hydrogen ions with other components.

$pH = -\log_{10} (a_{H^+}) = \log_{10} (1/a_{H^+})$, where a_{H^+} = activity of H^+ in mol/L thus pH units is always in log (L/mol). Activity can be defined as concentration of an ion multiplied by activity coefficient. For dilute solutions, activity coefficient is an actual number ranging

from 0 to 1 and greater than 1 for concentrated solutions. The coefficient is dependent on nature of ion, temperature, ion force and many other solution parameters. For a strong electrolyte, activity of an ion approaches its concentration in dilute solutions (Bruch, 2005). NEMA max allowable level is 6.5 – 8.5.

2.2.4 *E-coli*

Fecal coliforms are bacteria that generally live in animal and human intestinal tracts and are linked with animal or human wastes. Its detection in drinking water is a clear indication of current water contamination by sewage or animal wastes. *E. coli* originates from animal and human wastes and it gets into water bodies during different types of precipitation which include; rainfalls and snow melts. Once these waters are consumed without adequate treatment, *E. coli* ends up in this water. Most *E. coli* are harmless but some can lead to severe diarrhea. Some coli like K coli bacteria causes severe anemia, kidney failure and even death in extreme cases. Other strains of *E. coli* can result in urinary tract infections or other infections (McGlade, 2012).

Children below five years old and the elderly are the most susceptible to *E. coli* where it causes hemolytic uremic syndrome infection. A study conducted in the United States indicated that hemolytic uremic syndrome caused by *E. coli* 0157:H7 was found to be the main cause of acute kidney failure in children (Davis, 1968). The syndrome is a life-threatening illness which requires blood transfusions and kidney dialysis. The rate of death for hemolytic uremic syndrome (red blood cells impairment) is 3-5% and in adverse *E. coil*, feeling weak, pale skin, bruising and passing small amounts of urine will

be the major symptoms (Schwartz, 1935). NEMA requires a maximum allowable limit of NIL/100 mL.

2.2.5 Ammonia and ammonium

Sources of ammonia in the environment can be either from surface water or rain water with the concentration of ammonia in surface water varying according to the region and season. Ammonia sources can also be affected by anthropogenic activities which include agricultural runoff and industrial discharge from sewage treatment plants. In bays and rivers, ammonia concentration is always less than 6 mg/L and if it is more than this value, it points to anthropogenic pollution (Bouwer and Crowe, 1988). Natural ammonia concentrations especially in ground water are generally less than 0.2 mg/L. However, deep wells which have been exposed to geological formations have indicated high levels of ammonia (Schilling, 2002). Ammonium ion in water is usually in equilibrium with ammonia and this equilibrium is dependent on pH and, to certain degree, temperature. In acidic or neutral water the equilibrium generally favours the ammonium ion. Under the influence of pH, temperature, wind speed and atmospheric ammonia concentration, ammonia can partially undergo volatilization from surface water to the atmosphere. Ammonia in the environment can be removed in different ways. Since it is extremely soluble in water, amounts in air can be dissolved in rainwater. It can also be removed by adsorption on sediment and suspended organic material or in microbial processes. In water sources like surface water or groundwater, ammonia can go through a series of changes which involves two processes in the nitrogen cycle; nitrification and denitrification. During nitrification, nitrite and nitrate are formed from the aerobic

process which is later taken up by aquatic plants and other organisms while during denitrification, which involves anaerobic process, elemental nitrogen is formed which is later lost to the atmosphere through volatilization.

Ammonium is an ion whose presence in the environment is mainly through the application of fertilizers. A proposal was made for threshold of ammonium cation to be 35 mg/L. Ammonium can be used in production of fertilizer and animal feeds, manufacture of paper, plastics, fibers, rubber and explosives. It can also be used in metal processing, as a coolant and a starting material for nitrogen containing compounds (Holleman, 1985). Other uses of ammonium compounds include ammonium chloride used as a diuretic and as cleansing agents and food additives. Ammonia and ammonium cation can be determined by indophenol reaction at a concentration between 0.025 and 3 mg/L and by use of ammonium-ion selective electrode which is less sensitive. At a concentration higher than the ability to be detoxified, ammonium can cause a toxic effect on healthy humans. Ammonium chloride can lead to interference in metabolism at a concentration exceeding 100 mg/Kg of body weight per day, shifting of acid-base equilibrium, reduced tissue sensitivity to insulin and it affects glucose tolerance (WHO, 1996).

2.2.6 Metal ions

2.2.6.1 Lead

Lead (Pb) with atomic number 82, is a metal that is bluish-white, lustrous in appearance and has an atomic mass of 207.2 amu with a melting point of 327.5°C. It is very soft, ductile, very malleable, and poor in conducting electricity. Lead has a boiling

point of 1749°C and it does not corrode but it can blemish once it is exposed to air. It is found in natural deposits as *galena* (lead sulphide), *cerrusite* (lead carbonate) and is regularly used in lead-acid batteries, construction industry, alloys for X-ray shield, household plumbing materials, soldering and water service lines. One can be exposed to lead through inhalation and ingestion as a salt or in elemental form and it hardly gets into water sources but can enter drinking water through corrosion of plumbing materials. Once in drinking water at a concentration exceeding maximum limits, lead can lead to serious health effects like underdevelopment of the body both physically and mentally. It also affects learning abilities in babies and children (Drelich, 2011). In adults, high lead concentrations can lead to increase in blood pressure and if exposed over a long period, it can lead to kidney problems. The WHO recommends a maximum limit of 0.01mg/L for lead in drinking water (WHO, 2003). NEMA guideline value is 0.05 mg/L.

Children below 6 years old and pregnant women are the most susceptible people to lead. Children's susceptibility to lead is due to their ability to absorb 4-5 times more lead than adults. Also there is a placental transmission of lead in humans as early as the 12th week of conception and these remain throughout the embryonic development process. Lead is a toxicant commonly known to accumulate in the skeleton.

2.2.6.2 Zinc

Zinc (Zn) is a metal with atomic number 30 and atomic mass of 65.39 amu. It is bluish in color, has a melting point of 419.58°C and a density of 7.133 g/cm³ at a temperature of 293K. It occurs in traces mostly in the igneous rocks with sulfides. Sphalerite and wurzite are the main zinc ores (Elinder, 1914). Naturally zinc content is

estimated to range from 1-300 mg/kg dry weight in soil (Nriagu, 1980). Approximately a small percentage (5%) of a population is capable of differentiating between zinc contaminated water at a concentration of 4mg/L and zinc-free water. At a concentration ranging between 3-5 mg/L, zinc's exposure to heat makes it develop a greasy film and makes water appear opalescent (Cohen, 1960).

Zinc and its products can be used in different areas in the production of brass and alloys which are resistant to corrosion and also for galvanizing products made of iron and steel. Zinc oxide which is the most used compound is used in rubber manufacturing as a white pigment while oral zinc is used in the treatment of zinc deficiency in humans. On the other hand zinc carbamate is used for its pesticidal property as a pesticide (Elinder, 1914).

The commonly used method for determining zinc is atomic absorption spectrophotometry. This method (detection limit of 50µg/L) uses direct air-acetylene flame for analysis. Zinc can be determined by chelation of zinc with ammonium pyrrolidine dithiocarbamate followed by use of methyl isobutyl ketone for extraction process (detection limit 0.5–1 µg/L). Zinc concentrations in water varies according to water sources where by its concentration is generally 10 µg/L in natural surface water, 10–40 µg/L in ground water and concentration in tap water is likely to be more due to zinc leaching from pipes and fittings (Elinder, 1914). At low pH, we have low mineral salt content and high carbon dioxide content. Zinc's maximum allowable limit according to NEMA is 1.5 mg/L in drinking water. WHO initially gave a guideline value of 5 mg/L in 1984 which was abandoned in 1993. A concentration that is higher than 3 mg/L is however not palatable to most humans. Ingestion of zinc salts in dietary supplement or

emetic exceeding maximum allowable limits can lead to acute toxicity while ingestion of concentration more than 500 mg of zinc sulfate causes vomiting. Beverages and food poisoning have been reported with drinking acidic beverages packed in galvanized zinc containers. This led to health problems like vomiting, nausea, fever, stomach cramps and diarrhea within 3-12 hours of drinking. (Elinder, 1914).

2.2.6.3 Potassium

Potassium is one of the essential elements in human which is found in the environment and whose presence in drinking water can be due to use of potassium permanganate in water treatment as an oxidant. Potassium exists in both animal and plant tissues and is termed as very essential. Diet is the main source of potassium for the general population, as the element exists in most foods especially vegetables and fruits. It is also found in food additives and as medicated potassium supplements (WHO, 2009). Potassium chloride can be used as an alternative for sodium chloride in ion exchange for household water softening where potassium ions are likely to exchange with calcium and magnesium ions. Suggestions have been given out for replacement of sodium salts with potassium salts for water desalination conditioning or partial replacement although partial replacement seems to be improbable due to cost difference (WHO, 2009). This ion has no guideline value.

2.2.6.4 Sodium

Sodium ion in surface and ground water originates from dissolution of sodium salts found in rocks and soil. The concentrations of sodium in water sources vary as

follows: seawater 11,000 ppm, river waters 9 ppm and drinking water contain 50 ppm. Sodium exists mostly as sodium chloride which is soluble. Based on taste, the recommended maximum limit for sodium in water is 200 mg/L. No guideline value exists for WHO and NEMA (WHO, 1996).

2.2.7 Nitrates

Nitrates are naturally occurring chemical substances found in the soil which is always in form of nitrogen. They are formed from breaking down of fertilizers, organic residues or decaying plants by microorganisms. In the environment, nitrate can be expressed in form of nitrate (NO_3^-) or nitrate-nitrogen ($\text{NO}_3\text{-N}$). The compound exists in some ground water and is important to most crop plants which require large amount of nitrate to sustain high yield. Consequently, plants may accumulate it in their stems and leaves. In a reasonable concentration, nitrate is not a harmful constituent of food and water but at a high concentration it may lead to adverse health effects in infants like blue baby syndrome or methaemoglobinaemia (whereby the less strong acidic nature of an infant stomach converts nitrates to nitrites). Also at high nitrates concentration intake, pregnant women, adults with less stomach acidity and people deficient in the conversion enzyme are susceptible to nitrite-induced methaemoglobinaemia (conversion of methaemoglobinaemia back to normal haemoglobin (Stanton, 1992; Self and Waskom, 2008).

The development of nitrates is a very basic part of the nitrogen cycle in the environment. Once in the environment, the compound can leach into ground water by rain or irrigation water. Another source of nitrates in the environment can be

anthropogenic sources. The human activities contribute to high amounts of nitrates in the environment compared to natural sources like municipal waste and sludge, fertilizers and manure, septic systems, animal feedlots and nitrogen-fixation from atmosphere by legumes, bacteria and lightning (Soltanpour et al, 1999). WHO has a guideline value of 50 mg/L with NEMA having a value of 10 mg/L.

2.2.8 Fluorides

Fluoride is a naturally occurring ion found in the Earth's crust and is derived from fluoride salts. It is considered as essential for human health. It is formed from natural or through anthropogenic activities. Fluoride is found in water through chemical weathering of rocks containing fluoride rich minerals like biotite, apatite homblende and fluorite (WHO, 2004). Anthropogenic sources adding it to water includes application of phosphate fertilizers and deposition of electronic waste materials (Gleick, 1993). Several factors determine the abundance of fluoride in water. Lower amounts of calcium and magnesium in water always leads to lower fluoride content. Fertilizers and farming activities from anthropogenic inputs also increases the amount of fluoride in water. WHO recommends a concentration of 1.5 mg/L fluoride in drinking water and at a concentration exceeding this value poses a health risk (dental and skeletal fluorosis) to those relying on underground water for drinking.

Water is an important natural resource and its over exploitation and misuse is of serious concern. The quality of surface water can potentially be affected by either natural causes or anthropogenic where natural causes can be through precipitation, soil erosion

and lithological alteration. Anthropogenic sources can be linked with urban development, agriculture and industry (WHO, 2004). Figure 2.1 shows an example of dental fluorosis.



Figure 2.1. Dental fluorosis

2.2.9 Chlorides

Chloride is a naturally occurring ion whose distribution in nature originates from salts like sodium chloride (NaCl), calcium chloride (CaCl₂) and potassium chloride (KCl) just to mention a few. Its taste threshold in water depends on the cation. For sodium and calcium chloride, taste threshold in water ranges from 200—300mg/L (Zoeteman, 1980). Taste of coffee prepared with water containing 400 mg/L sodium chloride concentration or 530 mg/L calcium chloride concentration can easily be affected. Sources of chlorides in the environment are introduced through natural activities. Natural sources include weathering of rocks which exposes chlorides hence leaching into soil and water. This is indeed made easier due to high solubility of sodium chloride. WHO has recommended a maximum limit of a total intake of 530 mg/day of chloride for adults and 45 mg/day for children up to 18 years old. A research by WHO reported that a dose of 1 g of sodium chloride per kg body weight is lethal for a 9-week-old child (WHO, 2003).

In the recent research, chloride's toxic effect in humans has not been observed apart from a special case where there was a congestive heart failure caused by impairment of sodium chloride metabolism (Wesson, 1969). The body of a healthy person can survive the high chloride intake so long as there is an immediate follow up of

intake of fresh water. Much has not been found on the adverse effects to human beings as a result of a prolonged intake of significant amount of chloride. But in an experiment performed in animals sodium was found to cause hypertension rather than chloride ion. The other disadvantage of chloride in water is that it can lead to increase in corrosiveness as a result of increase in water electrical conductivity. Chloride reacts with metal pipes with the formation of a soluble salt. Consequently this increases metal ion concentration in drinking water. This process of chloride dissolution enhances the galvanic corrosion (Gregory, 1990). A WHO guideline value is 250 mg/L. There is no NEMA guideline value.

2.3 Instrumentation

2.3.1 Total reflection x-ray fluorescence spectroscopy

The S2 PICOFOX (Klockenkamper, 1997; Reinold and Alex; Klockenkamper et al, 1992) is the initial portable bench top spectrometer in the world which operates on the principle of total reflection X-ray fluorescence spectroscopy that involves microanalysis (fast quantitative and semi-quantitative multi element) of liquids, suspensions and solids. Reaching detection limits in the ppb and ppm range, the S2 PICOFOX is optimally suited for trace element analysis. The spectrophotometer also analyses liquids, powders and solid samples using the same principle as for microanalysis.

Contrary to other analytical methods, spectrometer can detect trace elements in liquids up to concentrations lower than 0.1 ppb and also quantitative results can be obtained from samples containing a concentration as low as ng to μg . The compact S2 PICOFOX instrument is designed in such a way that it can be used in both field and on

site measurements. S2 PICOFOX operates with minimum expenses on consumptions of gases or liquid nitrogen but all it needs is a source of power and its first results are available within minutes (Beckoff *et. al*, 2007).

2.3.1.1 Key advantages of total reflection x-ray compared to XRF spectrometers

Comparing S2 PICOFOX to XRF spectrophotometer, S2 PICOFOX uses monochromatic radiation and total reflection optics hence the following advantages: Detection limits reduces to 0.1 ppb due to enhanced fluorescence yield and reduced background noise; simple quantification is allowed due to reduced absorption and scattering effects in the sample matrix; there is higher sensitivity to the elements present in trace amounts and it can analyze a concentration of a sample amount as small as nanogram or microgram range.

2.3.1.2 Key advantages compared to atomic spectroscopy methods (e.g. AAS, ICP-OES)

Comparing S2 PICOFOX to AAS, S2 PICOFOX has the possibility to measure samples directly, mostly without digestion and provides instant results of even unknown samples. The advantages include: Simultaneous multi-element trace analysis including halogenides; it extends linear concentration range from ppb to percent; lower cost of operation ; it can analyze samples with small concentrations, partly nondestructive; it uses an internal standard to perform quantification; it is suitable for many types of samples and applications (liquids, suspensions, solid materials, thin films, filters or

contaminants); it has a portable system for fast in-field analyses and a robust technology which can be used for training students. The schematic diagram is shown in Fig. 2.2 .

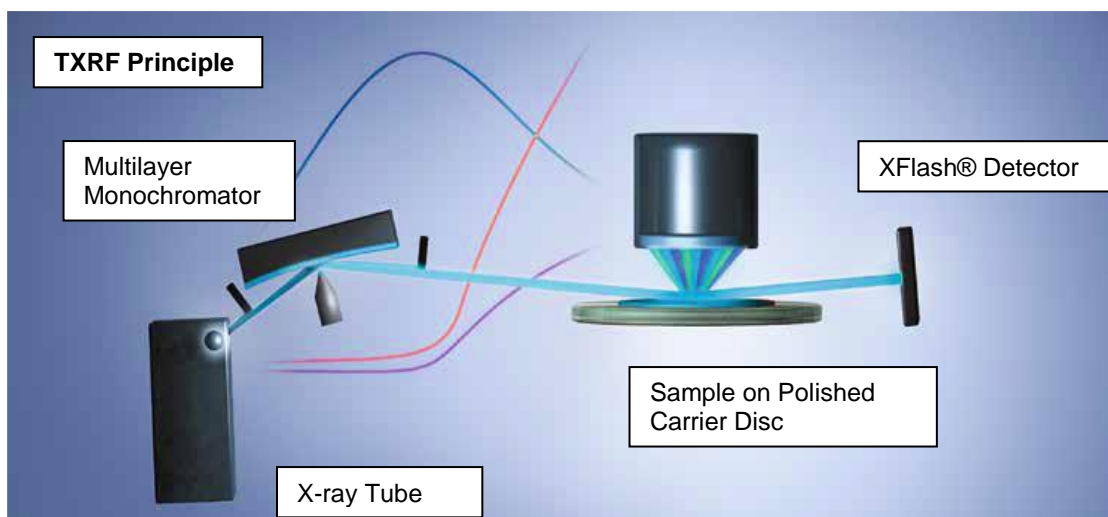


Figure 2.2 : Schematic diagram of TXRF (Klockenkamper, 1997)

As mentioned earlier, the working principle of S2 PICOFOX is conventional on that of total reflection X-ray fluorescence (TXRF) analysis method. This principle works as follows; An X-ray tube which is cooled using air and has a molybdenum target produces an X-ray beam which by use of a multi-layer monochromator, the beam is reduced to a narrow energy range (fine beam) which later intrudes on a refined sample carrier at an angle $< 0.1^\circ$ hence a full reflected beam. Specific fluorescence emitted by the sample is determined in a detector i.e. an energy dispersive X-ray detector. The short distance to the carrier leads to a high yield of the fluorescence hence a low absorption by air. TXRF and conventional XRF spectrometers differ mainly in the use of monochromatic radiation and total reflection optics. When the sample is illuminated with a full reflected beam, there is a reduction in absorption and scattering of the beam in the sample matrix hence significantly enhanced fluorescence yield, a substantial decrease in

background noise, and consequently much higher sensitivities to elements that occur only in traces.

2.3.1.3 How often is a calibration required?

The S2 PICOFOX does not need calibration; this is because it is factory-calibrated. Every day the instrument quantifies unknown samples hence use of gallium internal standard is mandatory. The intensity of the fluorescence of the element is always proportional to its concentration in the sample as a result of the thin layer. No further calibration of the instrument is required by the user due to the accuracy of the quantitative analysis in ppb.

2.3.2 Flame photometer:

2.3.2.1 Principle of operation:

Alkali and alkaline earth metals can be analyzed by a flame photometer. These metals are dissociated by heat from the flame producing atoms. Some of the atoms can further undergo excitement to a much higher energy level-hence the working principle of flame photometry. When the atoms at the higher energy level returns to the ground states, a radiation is emitted (at a wavelength specific for the element analyzed) which lies in the visible area of the spectrum. Table 2.1 presents details of the measurable atomic flame emission wavelengths and flame colour of the alkali and alkaline earth metals (Chatwal and Anand, 2002; Deans and Rains, 1971).

Table 2.1: Details of the emission wavelength and the color produced

Element	Emission Wavelength (nm)	Flame Colour
Sodium (Na)	589	Yellow
Potassium (K)	766	Violet
Barium (Ba)	554	Lime Green
Calcium (Ca)	622	Orange
Lithium (Li)	670	Red

At a certain range of concentration, the intensity of emission is directly related to amount of atoms coming back to the ground state. Consequently, this is proportional to the total amount of the volatilized species in the flame hence making the emitted light in the flame photometer directly proportional to the concentration of the sample. Electrical signal which is also proportional to the concentration of the sample can be acquired by the isolation of the emitted light at a characteristic wavelength using an optical filter followed by the measure of the light intensity determined using a photo-detector. The electrical signal can be obtained and the readout done in analogue or digital form after processing.

2.3.2.2 Instrumentation:

The basic components of a simple flame photometer include: Burner that provides a flame whose form and temperature is constantly maintained; Nebulizer and mixing

chamber which provides a pathway through which a homogeneous solution is transferred into the flame at a steady rate; color filters which separates light of the wavelength to be determined from that of extraneous emissions; photo-detector that acts by determining the intensity of radiation emitted by the flame. The Figure 2.3 is a simplified outline of the instrumentation indicating its components.

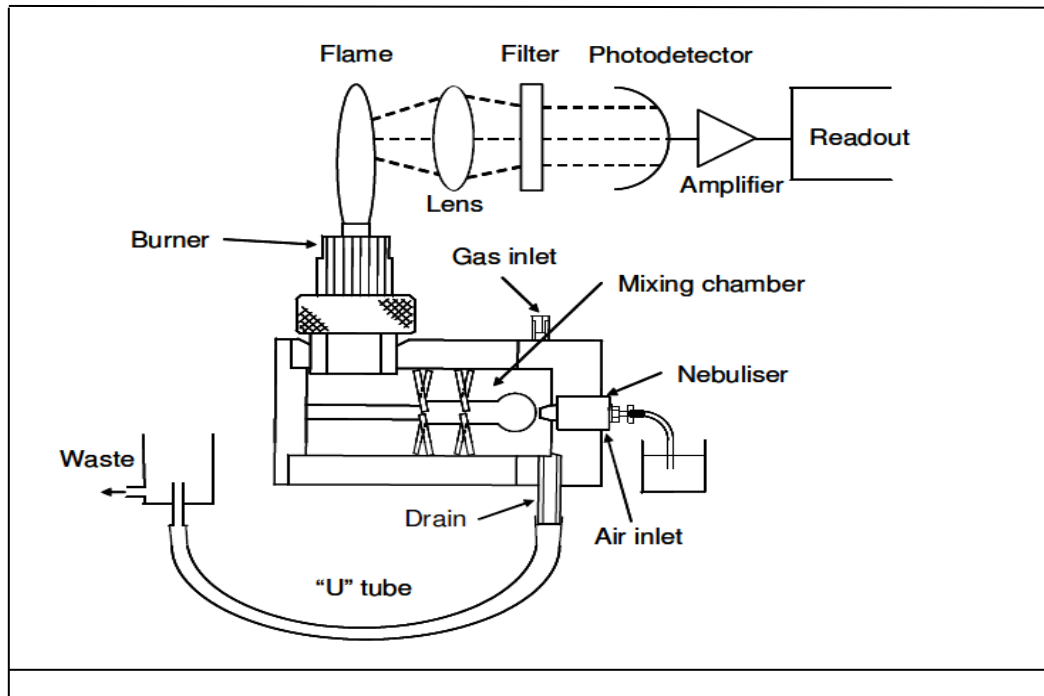


Figure 2.3: Schematic diagram showing the component parts of a flame photometer (Flame photometer, 2009)

Analyzing alkali and alkaline earth metals by use of a flame photometry method has two advantages which include: low temperatures for its operation and the metals have a wide spectrum due to their characteristic wavelengths hence making them easier to be isolated from those of most other elements.

2.3.2.3 Disadvantages:

This technique can be affected by temperature. This is because intensity of emission is very sensitive to changes in temperature of the flame. Normally there is an encounter of spectral interference and self-absorption which affects the precision of the measurement and also a straight line is not obtained when absorbance against concentration curve is plotted.

2.3.2.4 Applications:

The flame photometer is used entirely in the quantitative determination of metals in solution, especially alkali and alkaline earth in the given samples. It uses the same principle as that described for AAS. It can also do qualitative analysis as each element emits its own characteristic line spectrum.

2.3.3 UV-Visible Spectrophotometer

Ultraviolet-visible spectroscopy/spectrophotometry (UV-Vis) is a technique that uses radiation in the range 190 nm to 800 nm (Pavia et. al., 1996; Jaffe and Orchin, 1962; Kalsi, 2004; Misra and Dubinskii, 2002). The UV range is from 200-400 nm while the visible range is from 400-800 nm. In the visible range is where the supposed color of the ion involved is affected by the absorption or reflectance processes. In the area of electromagnetic spectrum, molecules are likely to undergo electronic transitions. In UV-Vis spectroscopy, there is occurrence of transitions from ground state to excited states from highest occupied molecular orbital to the lowest unoccupied molecular orbitals. The occupied orbitals are sigma, pi and the non-bonding.

Spectrophotometer is an instrument used to measure the proportion of transmitted of light that is absorbed. Molecules with bonding electrons (π) or non-bonding electrons (n-electrons) are capable of absorbing energy in form of ultraviolet or visible light exciting these electrons to higher anti-bonding molecular orbitals. The wavelength absorbed is dependent on how easily the electrons are excited i.e. the faster the excitement of electrons the longer the wavelength of light absorbed. The spectrophotometer can determine a concentration of the unknown sample in two ways: generation of a standard curve of absorbance against concentration. The absorbance obtained is then compared to the standard curve; use of the Beer-Lambert's law which involves drawing of a standard curve indicating a linear relationship between absorbance and concentration where the wavelength at which a substance absorbs best (λ_{\max}) is determined. Beer Lambert's law is considered to be a fundamental law which rules the quantitative spectrometric analysis. The name is a combination of two laws.

2.3.3.1 Lambert's law

This law explains how the intensity of a beam of a parallel monochromatic radiation reduces sharply as it passes through a medium of homogeneous thickness.

2.3.3.2 Beer's law

This law explains the direct proportionality of the absorbance of a solution with the concentration of the absorbing species in the solution and the path length. At a fixed path length, concentration of the absorber can be determined by a UV/Vis spectroscopy.

Hence Beer-Lambert's law can be expressed as:

$$A = a b c$$

Where,

A- is the absorbance or optical density ; a –is constant, which is the absorptivity or extinction coefficient; b- is the path length of radiation through sample in cm; c- concentration of solute in solution. Hence absorbance A is directly proportional to the concentration c. Determination of the transmittance or absorbance of a sample as a function of the wavelength of electromagnetic radiation is done by a spectrophotometer. The basic components of a simple spectrophotometer include: radiation source; dispersion device selector (selects a specific wavelength from the broadband radiation); monochromator; sample area port and detector. Fig 2.4 shows the schematic diagram of a UV-VIS spectrophotometer.

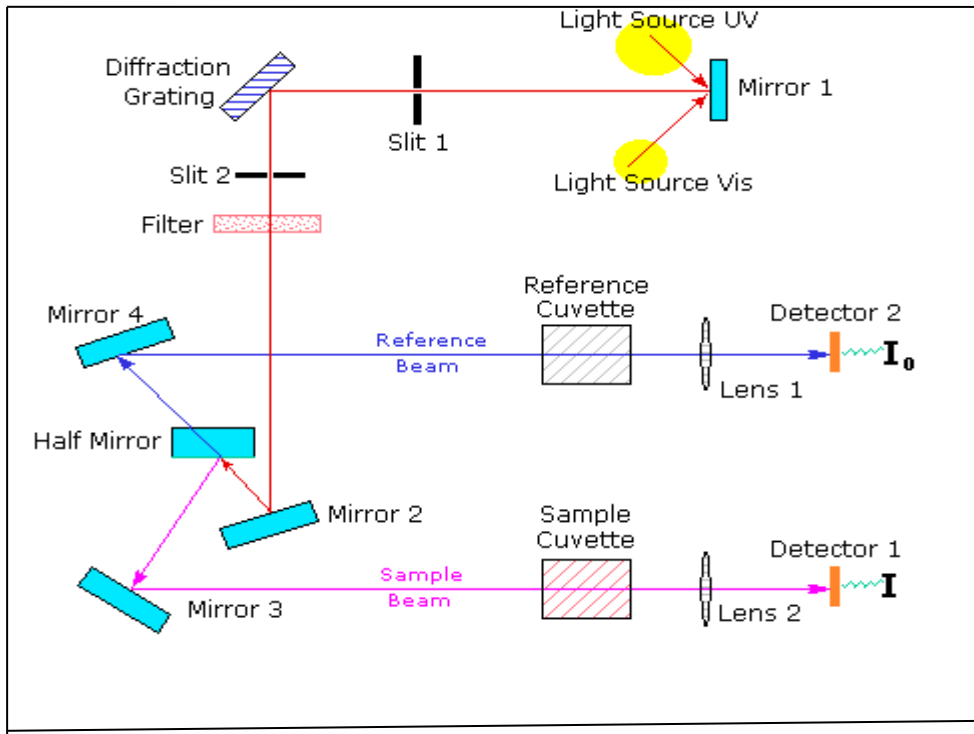


Figure 2.4: Schematic diagram showing the component parts of UV-VIS spectrophotometer (Misra and Dubinskii, 2002).

The higher resolution of the obtained spectra increases demands on the wavelength reproducibility of the spectrophotometer. The UV/VIS radiation after production by tungsten passes through a filter to the monochromator. This radiation is then passed through a beam splitter, with one passing through the sample and the other one going through the reference cuvette. Both beams reach the photodiodes where processing of the data is done. If the sample compound absorbs light then I is less than I_0 , and this difference may be plotted on a graph versus wavelength by a recorder.

2.3.3.3 Applications of UV-Vis spectrophotometer

The obtained spectra from the UV-Vis spectrophotometer can be applied in enhancing variances among spectra, resolution of overlapping bands in qualitative analysis and reduction of scattering and matrix interference effects in quantitative analysis.

2.3.4 Atomic Absorption Spectroscopy

2.3.4.1 Theory of AAS

Atomic absorption spectrophotometer (AAS) (Hargis, 1988; Kenkel, 1994) is a spectroanalytical tool that is used in the determination of metals concentrations by absorption of radiation. The absorption of radiation by an element is directly proportional to its concentration. The electron of an atom that has been excited to higher energy level absorbs a defined quantity of energy. This energy is different for different elements. In AAS the atoms need to be broken into atoms for this electron excitation to occur. This is done by various flame types in an atomizer that gives different temperature ranges. Air-acetylene flame gives a temperature of about 2300°C. Nitrous oxide-acetylene flame on

the other hand gives a temperature of 2,700°C. A hollow cathode lamp is the source of radiation where high speed electrons will ionize argon in the lamp. The ionized argon ions will then be attracted at high speed towards the cathode which is made of the element in the analyte. When argon ions reach the cathode, atoms of the element at the cathode will absorb this energy and be excited. When these atoms go back to ground state, radiation will be emitted and it is this energy that will be used to excite the metal atoms in the atomizer. This light beam will then pass through a monochromator on the way to the detector (Skoog, 2007). The concentration of sample is directly proportional to the light absorbed as given by Beer-Lambert's law (Broekaert, 1998; L'vov, 2005). The schematic diagram of AAS is shown in Figure 2.5.

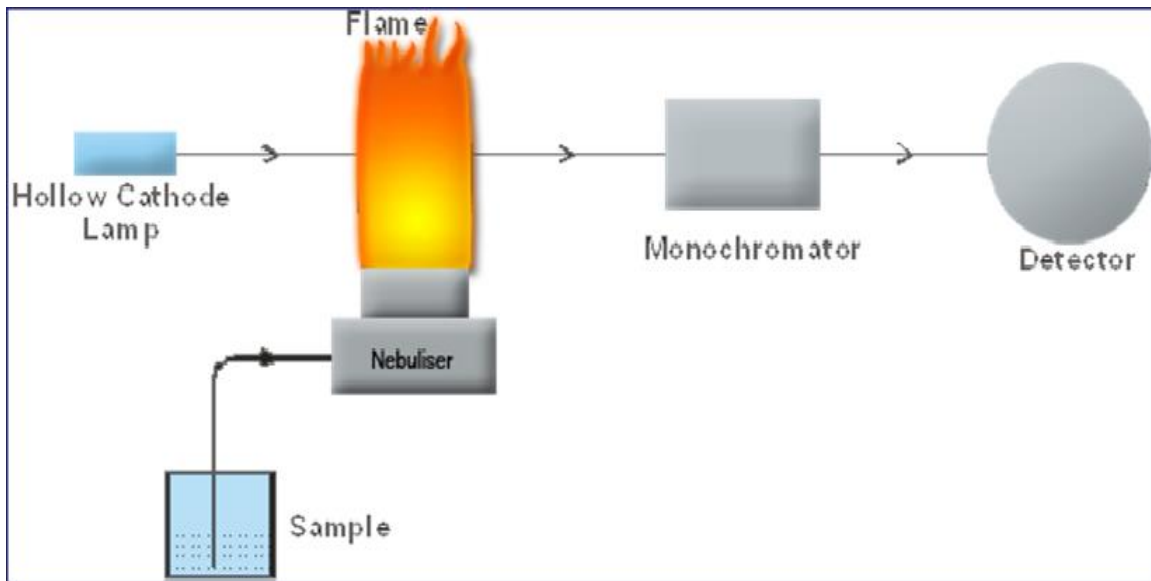


Figure 2.5 Schematic diagram of an AAS (Hargis, 1988; Kenkel, 1994).

2.3.4.2 Hollow Cathode Lamp

The hollow cathode lamp should have efficient emission of stable intense radiation. Compared with the width of the absorption lines to be determined, the resonance spectral lines should be narrow. The gas used in the cathode lamp is usually neon or argon and tungsten wire used as the anode. Cathode cup is made of an element whose spectrum is preferred hence for each element to be analyzed by AAS a different cathode lamp is required (Holte, 1993).

2.3.4.3 Chopper

This is a spinning wheel interposed amid the hollow cathode lamp and the flame in order to break the steady light from the lamp into an intermittent or pulsating light. This results in the production of a pulsating current which is amplified and recorded and thus the absorption of light will be measured without interference from the emitted light itself (NSW, 2003).

2.3.4.4 Nebulizer

The purpose of the nebulizer is to produce a mist or aerosol of the test solution. For a fine aerosol to be produced, a gas flowing at high pressure is required. The jet of air ventures by blowing across the capillary top hence the drawing up of the solution to be nebulized in the capillary tube takes place (Babcock and Walton, 2008).

2.3.4.5 Burner

In AAS, a burner is a source of heat which produces a flame that generates a temperature in excess of 2000K. Mostly this is obtained by burning the fuel gas in an oxidant gas i.e. nitrous oxide, air, or oxygen diluted with either nitrogen or argon. The flame produced is used for converting the liquid sample into gaseous state and similarly for conversion of the molecular entities into atomic vapor. A sample having metallic ion is aspirated into the flame. The flame breaks up the liquid into droplets which are then evaporated or burnt leaving the residue which is reduced to atoms (Katko, 2013).

2.3.4.6 Monochromator

The main function of the monochromator is selection and separation of a specific emission line from other lines. It also separates it from molecular band emissions. Advantage of diffraction gratings over prism is that it produces more uniformed dispersions. It therefore has higher resolution over a longer range of wavelengths (Skoog, 2007).

2.3.4.7 Detector

In improving the sensitivity of the spectra in the AAS, photomultipliers are employed. The detector produces an output which is then streamed to the right readout system. The source of the radiation received by the detector does not only come from selected resonance line but also come from the emission within the flame. The multiplier tube is most suitable for AAS. It has good stability if used with a stable power supply. It enables comparison of intensity lines in a satisfactory manner (Robbins, 2007).

2.3.4.8 Amplifier and Readout

Electric current from the photomultiplier detector is fed to the amplifier which highly increases the electric current. Generally lock in amplifiers are preferred which provides a very narrow frequency band pass and help to achieve an excellent signal to noise ratio (Hirsch, 1980).

2.3.4.9 Application of AAS

It is used for qualitative and quantitative analysis. Mostly it is used for quantitative analysis since the absorbance is proportional to the concentration of species. In this research work AAS was used to determine the quantity of heavy metals such as lead and cadmium.

CHAPTER THREE

METHODOLOGY

3.1 Sampling Sites

Figure 3.1 is a map of Mandera town showing the five sampling sites. It is situated in North Eastern, Kenya and the geographical co-ordinates of the sampling sites were as follows: Mandera Town, 3.926° N, 41.846° E.; Elwak, 3.914° N, 41.855° E; Shimbir Fatuma, 3.9093° N, 41.8392° E; Takaba, 3.914° N, 41.826° E and Banisa, 3.928° N, 41.835° E. The sampling sites are shown in Fig. 3.1.

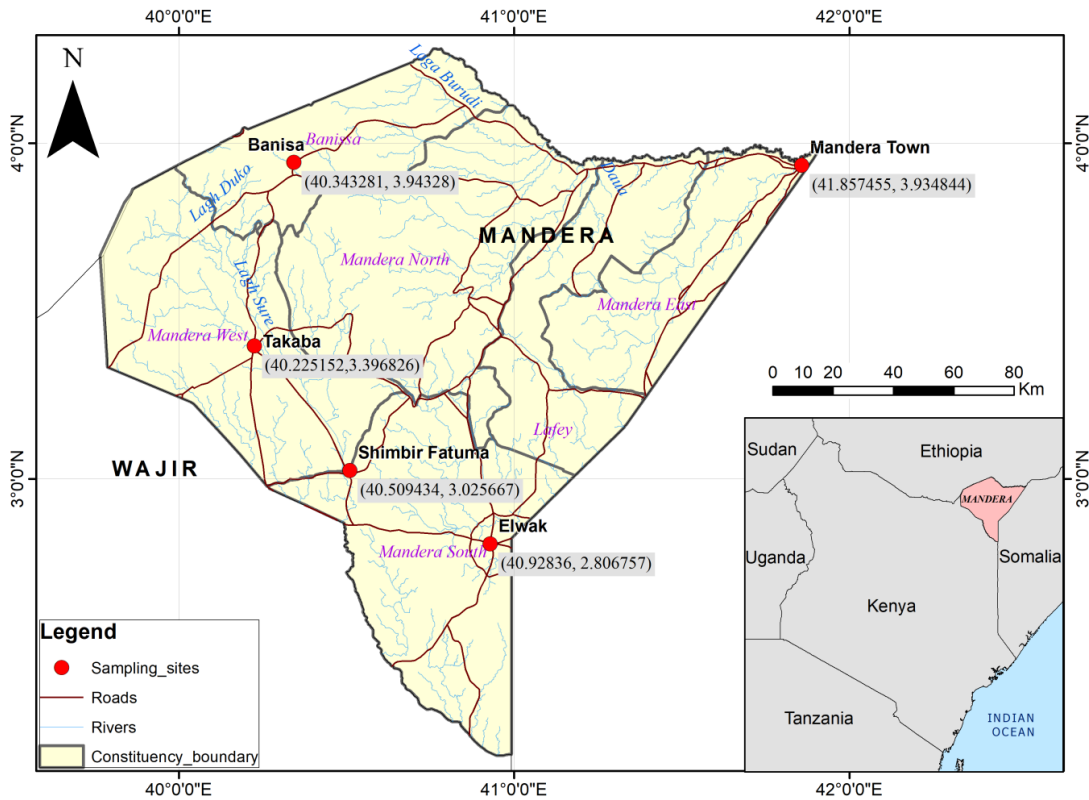


Figure 3.1. Map of sampling area in Mandera Town

Mandera County has three constituencies namely Mandera East, Mandera Central and Mandera West. Fig 3.2 shows constituencies in Mandera County.

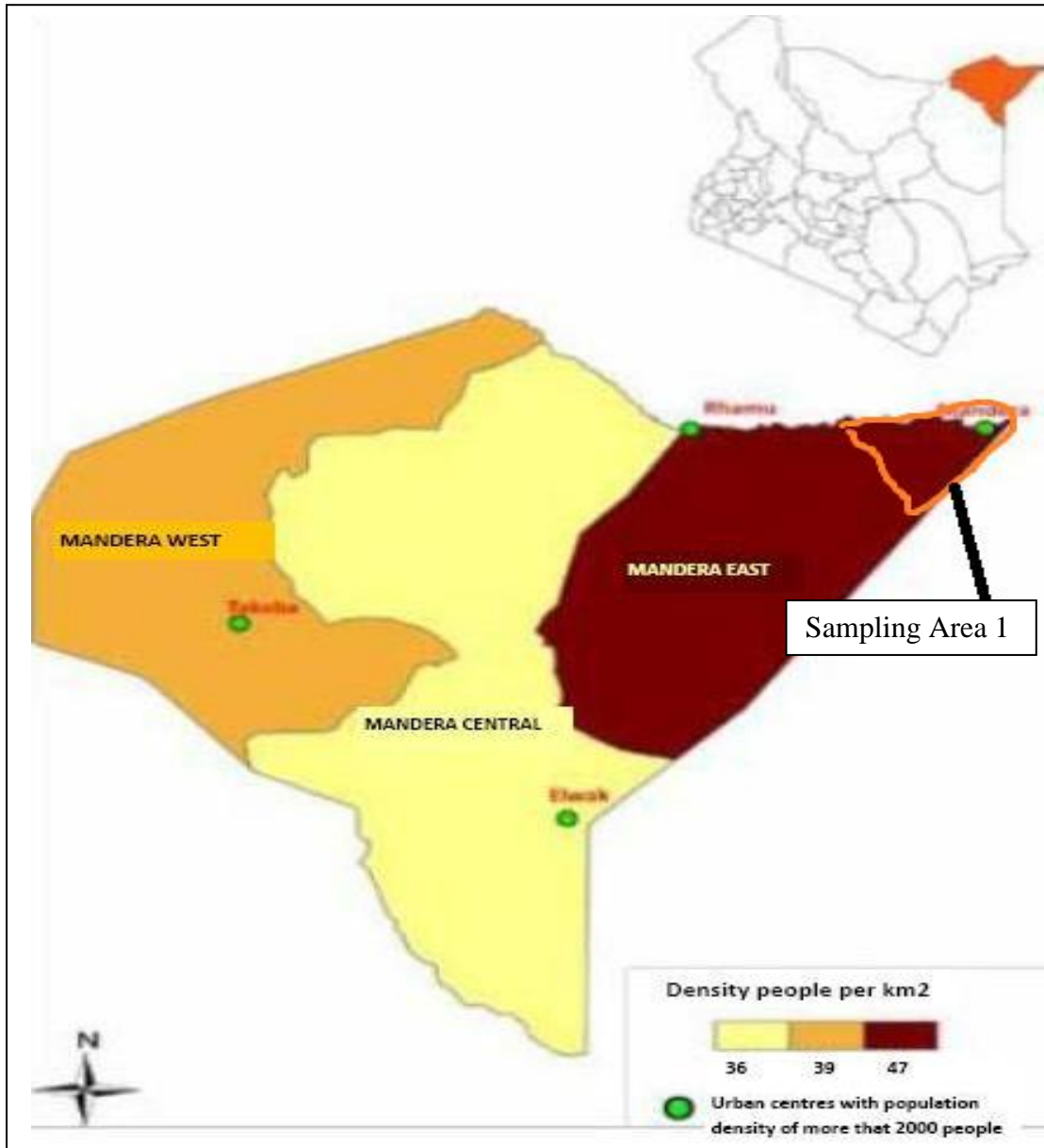


Figure 3.2: shows location of the map of the constituencies with respect to the sampling sites. Scale 1:500000

3.2 Instruments, chemicals and apparatus

3.2.1 Instruments

Total reflection x-ray fluorescence spectroscopy (S2 Picofox), Atomic Absorption Spectrophotometer (AAS)-6300 (Shimadzu, Japan), UV-Visible spectrophotometer model (UV-1700) (Shimadzu, Japan), Flame Photometer Model 410 (Sherwood), EC/pH meter model MI306 (Apps Enterprises Ltd, Australia), fluoride ion-selective electrode, pH meter model 15,(Fisher Scientific), Analytical balance and digital balance. The working condition of the atomic absorption spectrophotometer for the analysis of lead was as follows: Lamp current (5mA), wavelength (217.00 nm), slit width (1.00nm), fuel (acetylene), oxidant (air) and detection limit of 0.25ppm.

3.2.2 Chemicals and apparatus

Pipette (10mL, 25mL), Burette (50mL), beaker (200mL) , plastics bottles , 800 mL Kjeldahl flask, volumetric flask (100mL, 250mL), distilled water, lead nitrate, zinc sulphate, copper sulphate , standard potassium chloride solution with conductivity of 12.88 mS/cm, calcium carbonate, methyl red indicator, litmus paper indicator, phenolphthalein indicator, ethylenediaminetetracetic acid disodium salt decahydrate (EDTA), 1M hydrochloric acid, 1M sodium hydroxide, Nessler reagent, Erichrome black-T indicator, ammonia / ammonium chloride buffer, potassium chromate, sodium chloride, potassium chloride, filter paper No.1(James laboratory supplies).

3.3 Sample collection and storage

Sampling was carried out in different boreholes in Mandera town: Elwak, ShimbirFatuma, Takaba and Banisa in December 2014. The plastic containers were sterilized using hot deionised water. Three (3) litre plastic jars were used to collect and store the water samples. During collection, the tap was allowed to run for few minutes, then each container rinsed twice with the water and the containers were carefully filled with water and recapped. The samples were transported in a cooler box and later transported and preserved at a temperature of 4°C for bacteriological analysis. All the reagents that were used were of analytical and general purpose grade.

3.4 Determination of pH And electrical conductivity

An Exstik conductivity and pH meter was standardized using potassium chloride with conductivity of 12.88 mS/cm and calibration solution with pH = 7 respectively, at room temperature (25 C°). After this electrical conductivity mode was activated and electrode dipped in 40 mL of sample in a 100 mL beaker. The readings were taken in triplicate. The meter was then changed to pH mode and measurement taken again in triplicate.

3.5 Determination of Total Dissolved Solids (TDS)

A 100 mL of water sample was filtered through pre-weighed and washed beaker. The filtered sample in the beaker was then dried in an oven at 105°C for 5 to 6 hours to evaporate the water. The beaker was removed and placed into a desiccator to cool. The beaker and residue was then weighed and mass of the residue calculated in mg/L (WHO, 1996).

3.6 Determination of fluoride content

3.6.1 Buffer Solution

Approximately 500 mL of distilled water was transferred into a 1- liter beaker followed by an addition of 57 mL of glacial acetic acid, 58g of sodium chloride and 4g of ethylenediamine tetraacetic acid (EDTA). Magnetic Stirrer was used to dissolve the mixture then cooled to room temperature. Using 200 mL 5N sodium hydroxide, the pH of the solution was adjusted to between 5-5.5. The solution was later transferred to a volumetric flask (1 liter) and topped to the mark using distilled water.

3.6.2 Sodium fluoride, stock solution

2.210 g of sodium fluoride anhydride was weighed and transferred into a 1-liter volumetric flask. Deionised water was then added to dissolve the salt. The volume was then made to 1000 mL to make 1000ppm fluoride. From 1000 ppm dilution was made to give 100 ppm using dilution formula $c_1V_1=c_2V_2$ where c and v are concentration and volume respectively. From 100ppm a series of dilutions were done to give working standards: 0.5 ppm,1.0 ppm,2.0 ppm,4.0 ppm,8.0 ppm,10.0 ppm,20.0 ppm, 30.0 ppm, 40.0 ppm,50.0 ppm,60.0 ppm,70.0 ppm,80.0 ppm and 100.0 ppm of fluoride. The fluoride ion selective electrode was then calibrated. The different concentrations versus voltage in mV were then tabulated. 2 mL of the sample (each borehole sample) was then placed in a beaker and fluoride ion selective electrode dipped. The reading was then measured in mV. Using the straight line equation generated by the standards, the sample concentration was then calculated.

3.6.3 Chloride analytical procedure

The reagents for the determination of chloride concentration were prepared as follows:

3.6.3.1 Potassium chromate solution

K_2CrO_4 (1.0g) was weighed and placed in a 50 mL beaker. 20 mL of distilled water was added with stirring.

3.6.3.2 0.1M Sodium chloride solution

Sodium chloride (0.5873 g) was weighed and transferred into 100 mL volumetric flask. 40mL of distilled water was added to dissolve the salt. It was then made to volume using distilled water.

3.6.3.3 Standardization of silver nitrate solution with 0.1M NaCl

$AgNO_3$ (16.987g) was weighed and then transferred to a 1000 mL volumetric flask and made up to volume with distilled water. $AgNO_3$ solution was placed in a burette. Silver nitrate was standardized by placing 10 mL of 0.1M NaCl solution in conical flask and 2 mL of chromate solution was added. The solution was then titrated with silver nitrate until reddish coloration appeared. The amount of $AgNO_3$ solution used was recorded and the titration was repeated three times. The results obtained were recorded in a table and used to calculate the actual concentration of the $AgNO_3$.

3.6.3.4 Determination of chloride concentration

An aliquot of water (25 mL) borehole sample was pipetted into a clean 250 mL conical flask followed by an addition of 2mL K_2CrO_4 indicator. The solution was titrated with the standard $AgNO_3$ solution until reddish coloration appeared. The titration was repeated three times. The results obtained in each borehole were recorded (Kaur, 2008). This procedure was repeated for all borehole samples and the amount of chloride (mg/L) calculated.

3.7 Determination of ammonium in borehole water samples

3.7.1 Nessler's reagent

Into 1-liter volumetric flask, 100 g of mercuric iodide and 70g of potassium iodide were accurately weighed and placed into the flask followed by an addition of a small amount of distilled water. A cooled solution of 160 g of NaOH dissolved in 500 mL of distilled water was added to the mixture above then diluted to the mark. The reagent was stored in a Pyrex bottle out of direct sunlight.

3.7.2 Borate Buffer

Approximately 88 mL of 0.1N NaOH solution was added to 500 mL of 0.025M sodium tetraborate which was prepared by weighing 9.5g $Na_2B_4O_7 \cdot 10H_2O$ in a 1-litre volumetric flask. Stirring was done and volume made to 1 litre.

3.7.3 Sample preparation and procedure

A volume of sample (5 mL) was added to Kjeldahl flask followed by 5 mL of digesting solution and mixing done thoroughly. A small glass funnel was inserted in the mouth of the flask to prevent loss of liquid and for complete digestion to take place. Once the solution was clear, the mixture was gently heated under a hood and boiled briskly for some minutes and left to cool. Kjeldahl reagent blank was treated with 5 mL of the digested solution and simultaneously the contents transferred to a beaker for pH adjustment. The pH adjustment was done by adding about 35-36 mL 1N NaOH to neutralize the acid to pH 7. The neutralized sample was then transferred to a 100 mL volumetric flask and the solution diluted to the mark. From the diluted solution, 25 mL was placed in a 50 mL volumetric flask (Scheiner, 1975).

3.7.4 Ammonium chloride, stock solution

Ammonium chloride (3.819 g) was weighed and transferred into a 1 liter volumetric flask. Distilled water was then added and diluted to a volume of 1000 mL to make 1286 ppm of ammonium. From 1286 ppm dilution was made to give 129 ppm using dilution formula $c_1V_1=c_2V_2$ where c and v are concentration and volume respectively. From 129 ppm a series of dilutions were done to give standard: 0.13 ppm, 0.26 ppm, 0.39 ppm, 0.52 ppm, 0.64 ppm, 0.77 ppm, 0.90 ppm, 1.03 ppm, 1.16 ppm and 1.29 ppm of nitrogen using dilution formula $c_1V_1=c_2V_2$. The instrument was then calibrated. The absorbance values for the standards were determined and recorded. The sample was then run using UV spectrophotometer at a wavelength of 425nm.

3.8 Determination of nitrate

Nitrate ion in water boreholes was determined using sulphanilic acid method.

3.8.1 Preparation of nitrate standards

100 mL of each water sample was added to five separate beakers and dried in an oven at 105°C for 6 to 8 hours until dry. The beakers were then removed and kept in a desiccator and left to cool. The residue retained in the beaker was treated and the following dilutions made: 17mL of 0.1M AgNO₃ and 8mL of distilled water added to beaker one; 23mL of 0.1M AgNO₃ and 2mL of distilled water added to beaker two; 15mL of 0.1M AgNO₃ and 10mL of distilled water added to beaker three; 7mL of 0.1M AgNO₃ and 18 mL of distilled water added to beaker four; 9mL of 0.1M AgNO₃ and 16mL of distilled water added to beaker five; These were warmed using a heater then filtration was done. The filtrate was then dried in an oven at 120°C for 6 to 8 hours. The beakers were removed again and placed in a desiccator. 2 mL of sulphanilic acid was added to each beaker and 7mL of NH₄OH added. This was then transferred into 25mL volumetric flask then diluted up to the mark. Yellowish color was formed (Yang, 1998).

3.8.2 Preparation of stock solution

A volume of 2mL of 100 ppm nitrate solution was taken and put into a 100mL beaker and dried in an oven at 120°C for 4 up to 7 hours. 2mL of sulphanilic acid was added to dissolve the residue. 7mL of NH₄OH was then added and then diluted to 10 mL in a volumetric flask to obtain 20 ppm. From 20 ppm a series of dilutions were done to give working standards of 1.0 ppm, 2.0 ppm, 3.0 ppm, 4.0 ppm, 5.0 ppm, 6.0 ppm, 7.0 ppm, 8.0 ppm, 9.0 ppm and 10.0 ppm nitrate using dilution formula $c_1v_1=c_2v_2$. The

instrument was then calibrated. Then the samples were run using UV spectrophotometer at wavelength of 410nm (Yang, 1998).

3.9 Analyses of lead and zinc ions by Atomic absorption Spectrometer

3.9.1 Preparation of zinc metal ion standards

A stock solution 1000ppm (mg/L) of zinc metal ion solution was prepared by dissolving 0.442 g of hydrated zinc sulphate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) in 100 cm³ distilled water. Standard solutions of 0.1, 0.2, 0.4, 0.6 and 1.0 ppm were then prepared by serial dilutions. 0.1 ppm was prepared by taking 0.1 mL of 1000 ppm and then diluted to 1000 mL with deionized water in a volumetric flask. The other concentrations of 0.2, 0.4, 0.6 and 1.0 ppm were similarly prepared by separately taking 0.2, 0.4, 0.6 and 1.0 mL of the 1000 ppm stock solution and diluted to 1000 mL in a volumetric flask.

3.9.2 Preparation of lead metal ion standards

A stock solution 1000 ppm (mg/L) of lead metal ion solution was prepared by dissolving 0.162 g of lead nitrate (anhydrous) in 100 cm³ distilled water. Standard solutions of 0.25, 0.5, 1.0, 2.0 and 4.0 ppm were then prepared by serial dilutions. 0.25 ppm was prepared by taking 0.25 mL of 1000 ppm and then diluted to 1000 mL with deionized water in a volumetric flask. The other concentrations of 0.5, 1.0, 2.0 and 4.0 ppm were similarly prepared by separately taking 0.5, 1.0, 2.0 and 4.0 mL of the 1000 ppm stock solution and diluted to 1000 mL in a volumetric flask.

3.9.3 Digestion of borehole water samples

A sample (100 mL) of borehole water was added to a 250 mL conical flask. Concentrated nitric acid (5 mL, 67% concentrated) was then added to the sample and heated on a hot plate and evaporated to a volume of approximately 20 mL. The flask and its contents were allowed to cool. Nitric acid (5 mL) was again added and the mixture heated until about 10 mL of solution remained. It was then left to cool and filtered. The filtrate was then transferred into 100 mL volumetric flask. Distilled water was then added to volume. Air-acetylene flame was used with a hollow cathode tube lamp of lead or zinc used. A wavelength of 283.31 and 213.9 nm were used for lead and zinc respectively.

3.10 Determination of the concentration of sodium and potassium ion in borehole water samples

3.10.1 Sodium and potassium determination

NaCl (2.556 g) and of KCl (1.909g) were accurately weighed. Each was dissolved in distilled water to a volume of 1000 mL to make 1000 ppm of sodium and potassium respectively. From 1000 ppm dilution was made to give 100 ppm using dilution formula $c_1V_1=c_2V_2$ where c and v are concentration and volume respectively. 10 mL of each solution was pipetted from 100 ppm of each salt solution and added together in a 100 mL volumetric flask and diluted to the mark. A mixture of 10 ppm K^+ and 10 ppm Na^+ resulted. From 10 ppm of of the mixture of ions a series of dilutions were done to give working standards : 0.5 ppm, 1.0 ppm, 2.0 ppm, 4.0 ppm, 6.0 ppm, 8.0 ppm and 10.0 ppm using dilution formula $c_1V_1=c_2V_2$. The working condition of the flame photometer for the analysis of sodium and potassium were as follows: A flame of emission wavelength

of sodium (589 nm, yellow), emission wavelength of potassium (766 nm, violet); low temperature (1500-2000°C); suitable fuel mixture (propane/air and natural gas); and detection limit for sodium and potassium of 0.2 ppm.

3.11 Microbiological determination of water samples

3.11.1 Media Preparation

The preparation of the media used was done in applied biology laboratory at the University of Nairobi. An autoclave was used to do all sterilizations at a temperature of 121°C for 15 minutes and cleaning of working benches done by use of ethanol to ensure adequate sterility.

3.11.2 Preparation of MacConkey broth purple

MacConkey broth powder (8 g) was weighed and dissolved in 200mL of distilled water then heated until the media was dissolved completely. The solution was distributed into test tubes with inverted Durham's tube. Sterilization was done by autoclaving at 121°C for 15 minutes. For presumptive test 10 mL of lactose broth with inverted Durham's tube in test tube and inoculated with sample of water and incubated at the temperature of 37°C for 24 to 48 hours. There was turning of color for positive tubes from purple to yellow with gas produced at the Durham vials. The numbers of tubes showing acid and gas were noted and recorded. Examination of the colonies formed was done using an electron microscope. A loopful of metallic shine colony was transferred on nutrient agar plates and incubated at a temperature of 37°C for 24 to 48 hours.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Hydrogen Ion concentration (pH)

The pH of the water samples were found to be in the range of 5.1 to 7.67. The maximum value of pH was recorded at Elwak borehole (7.67) while the minimum value was recorded at Banisa borehole (5.1). The recommended limit of pH in water by WHO and NEMA is 6.5- 8.5. Table 4.1 below illustrates pH values for the different boreholes (Appendixes 1-5).

Table 4.1 pH value of water samples

BOREHOLE	pH	WHO	NEMA
Banisa	5.11 ±1.01	6.5-8.5	6.5-8.5
Takaba	7.13±1.13	6.5-8.5	6.5-8.5
Elwak	7.67±1.16	6.5-8.5	6.5-8.5
Mandera Town	5.30±1.20	6.5-8.5	6.5-8.5
Shimbir Fatuma	5.30±1.33	6.5-8.5	6.5-8.5

Takaba and Elwak boreholes were within the NEMA standards. However Banisa, Mandera and Shimbirwere below the NEMA standards. The pH at Banisa, Mandera Town and ShimbirFatuma could have had a low pH values due to more acidic rock composition. Graphic representation is shown in Fig. 4.1

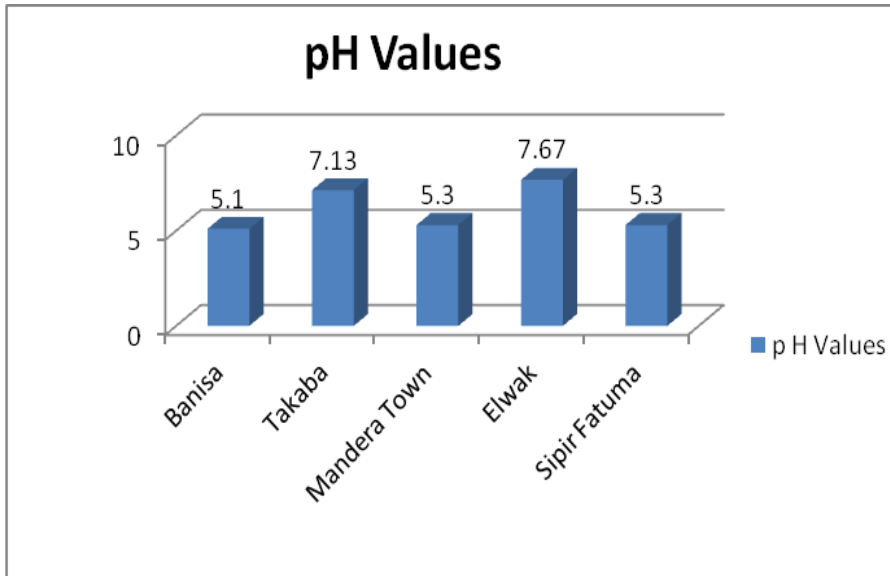


Fig 4.1. The pH values of water samples

4.2 Total Dissolved Solids (TDS)

The TDS values for the borehole water samples were from 520 mg/L to 4302 mg/L (Table 4.2). See Appendixes 1-5.

Table 4.2 TDS values of water samples

Borehole	Mass of beaker+sample (mg)	Mass of beaker (mg)	Mass of sample (mg)	TDS(mg/L)
Banisa	2304.6	2252.6	52.0	520.0
Takaba	2355.1	2252.6	102.5	1025.0
Elwak	2682.8	2252.6	430.2	4302.0
Mandera	2302.0	2252.6	49.4	494.0
Shimbir Fatuma	2321.2	2252.6	68.6	686.0

All boreholes samples were below the limit except for Elwak borehole which was slightly above the limit (4302mg/L). The acceptable NEMA limit is 1200mg/L. TDS is not a health hazard although high levels may indicate hard water which leads to scale build up in pipes. It can also cause salty or bitter taste in water. The residue per volume of the sample filtered and the result was expressed in mg/L.

The following formula was used to calculate the TDS:

$$\text{TDS, mg/L} = \frac{[(A-B) \times 1000]}{C}$$

Where:

A =(Weight of beaker + residue) in mg

B =Weight of empty beaker in mg

C =mL of sample filtered and dried

Volume of sample= 100mL

Fig. 4.2 shows TDS data in graphic form.

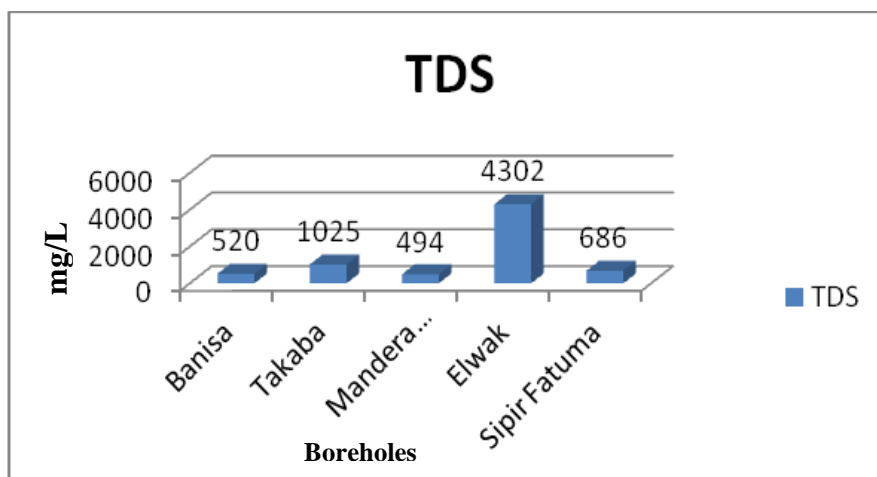


Figure 4.2. The TDS level (mg/L) in water samples

TDS in Elwak borehole could be higher due to presence of more soluble salts in the soil as compared to the other boreholes.

4.3 The electrical conductivity

Conductivity of water samples were found in the range 840-6940 $\mu\text{S}/\text{cm}$ (Table 4.3). Four boreholes values are within the range except for Elwak which was slightly above the WHO standards of $<2000 \mu\text{S}/\text{cm}$. Electrical conductivity is considered to be a rapid and good measure of dissolved solids (Appendixes 1-5).

Table 4.3 Electrical conductivity of water samples

BOREHOLE	EC $\mu\text{S}/\text{cm}$	WHO $\mu\text{S}/\text{cm}$	NEMA $\mu\text{S}/\text{cm}$
Banisa	840 \pm 10.2	2000	2400
Takaba	1654 \pm 15.6	2000	2400
Elwak	6940 \pm 19.2	2000	2400
Mandera Town	797 \pm 9.4	2000	2400
Shimbir Fatuma	686 \pm 10.1	2000	2400

Electrical conductivity has a direct relationship with TDS. Since TDS was also higher in Elwak it followed that electrical conductivity had to be higher as compared to the other boreholes. This data is shown in Fig. 4.3.

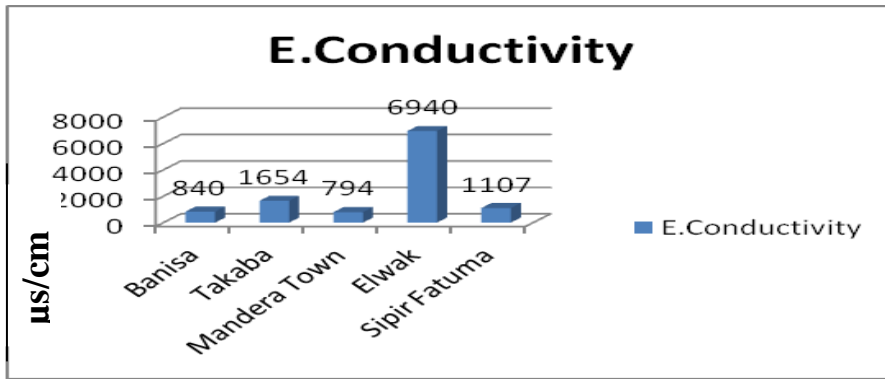


Figure 4.3: Electrical Conductivity ($\mu\text{S/cm}$) for water samples

4.4 Fluoride

Fluoride concentrations were found to range from 0.0 mg/L to 1.0 mg/L with the highest value (1.0mg/L) and the lowest value (0.0 mg/L) recorded at Mandera borehole and Banisa borehole respectively. These values were within the permissible limit of 1.5 mg/L as recommended by WHO and NEMA (Table 4.5). Table 4.4 shows the millivolt (mV) versus concentration for fluoride standards.

Table 4.4: Voltage in mV versus log of fluoride concentration of standards

S/NO:	Concentration of fluoride, x (ppm)	Log x,(where x=concentration)	Voltage in mV
1	0.50	-0.30103	126.0
2	1.00	0	113.2
3	2.00	0.30103	95.1
4	4.00	0.60206	78.5
5	8.00	0.90301	62.1
6	10.00	1	55.6
7	20.00	1.30103	39.0
8	30.00	1.47712	28.6
9	40.00	1.60206	20.9
10	50.00	1.69897	16.8
11	60.00	1.77812	11.6
12	70.00	1.84509	6.7
13	80.00	1.90309	4.9
14	100.00	2.00000	-0.9

Fig 4.4 shows a calibration graph for mV versus log of fluoride content in standards

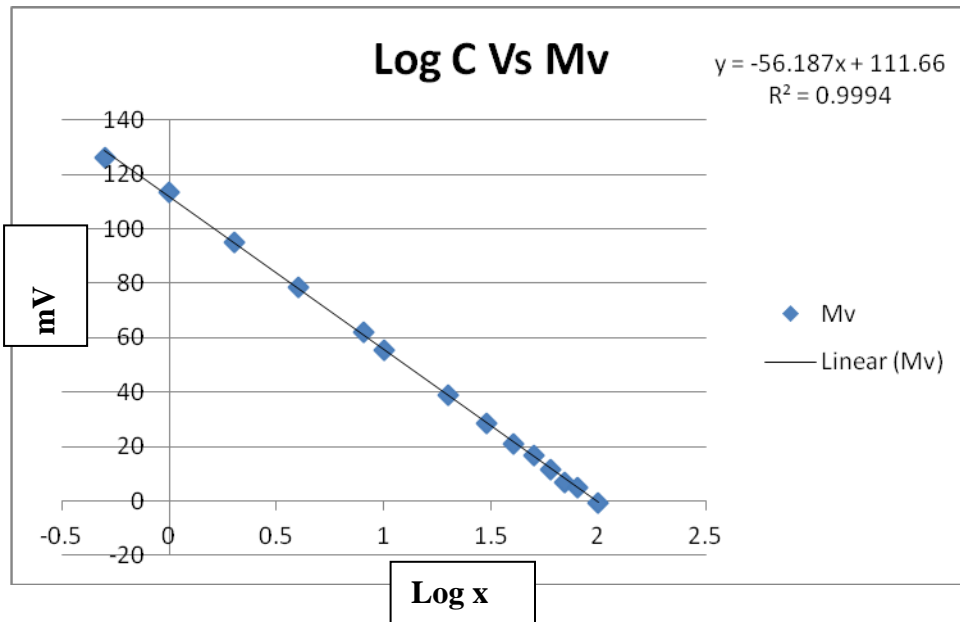


Figure 4.4: Calibration graph for fluoride standards

The equation in Fig. 4.4 ($y = -56.187x + 111.66$) was used to calculate the content of fluoride in the samples as given in Table 4.5. The values are also given in Appendixes 1-5.

Table 4.5 Fluoride concentration in borehole water samples

BOREHOLE	mV=y	Log x= $-(mV-111.66)/56.187$	x mg/L
Banisa	336.48	-4.000	0.00
Takaba	137.22	-0.455	0.35
Mandera Town	150.93	-0.699	0.20
Elwak	111.66	0.000	1.00
Shimbir Fatuma	124.13	-0.222	0.60

Fig 4.5 shows graphic data of fluoride content in borehole water samples.

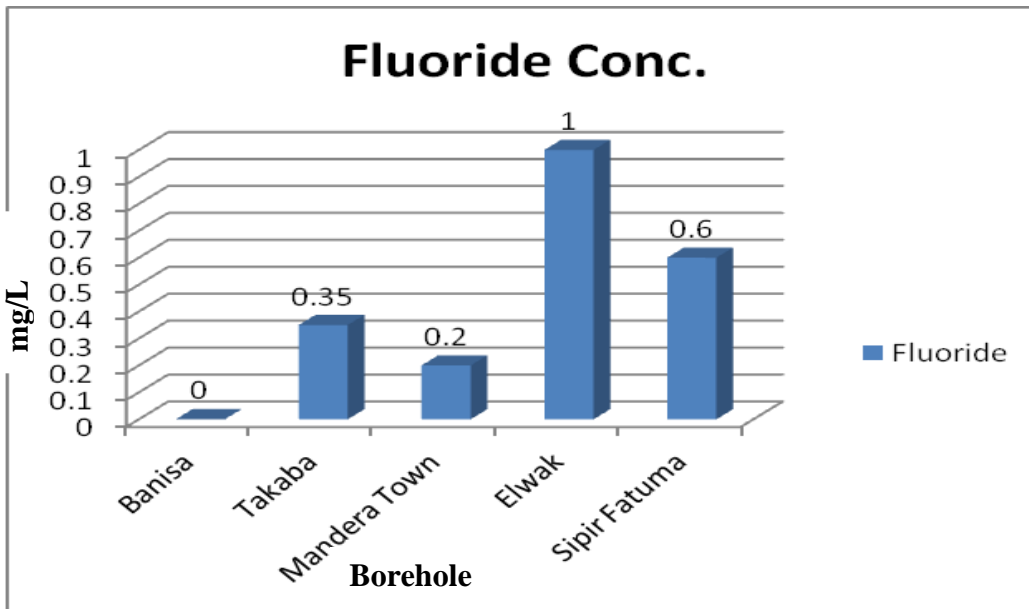


Figure 4.5: The level of fluoride ion (mg/L) in water samples

Elwak borehole had the highest fluoride concentration possibly due higher content of more soluble fluoride ores.

4.5 Chloride

The concentration of chloride was found to be in the range of 7.99 mg/L – 119.9 mg/L. Chloride values were within the acceptable NEMA and WHO limits of 250mg/L for domestic water. The highest concentration of chloride was obtained at Elwak borehole (119.9mg/L) and lowest at Shimbir(7.99 mg/L), as given in Table 4.12 (Appendixes 1-5). The chloride content was higher possibly due to presence of more soluble chloride salts in the borehole soil. Table 4.6 shows data for standardization of silver nitrate.

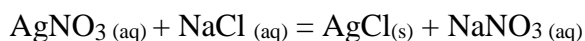
4.5.1 Standardization of silver nitrate solution with 0.1M NaCl

Table 4.6: Standardization of AgNO₃ with 0.1M NaCl

Burette reading	1	2	3	4
Initial burette reading (mL)	0.0	11.5	20.0	28.7
Final burette reading (mL)	11.4	20.0	28.7	37.4
Volume of AgNO ₃ used	11.4	8.5	8.7	8.7
Average volume of AgNO ₃ used	= 9.3 mL ± 1.2			

The volume of 0.1M NaCl used was 10 mL

Reaction stoichiometry between two salts is shown in scheme 4.1



Scheme 4.1: Reaction of silver nitrate with sodium chloride

Then moles of silver nitrate reacted with sodium chloride was calculated using the following formula:

$$\text{Number of moles of sodium chloride} = \frac{\text{Mass used}}{\text{Molecular weight}} = \frac{0.58730\text{g}}{58.44\text{g/mole}} = 0.01\text{mole}$$

$$\text{Molarity of NaCl} = \frac{1000 \times \text{mole}}{\text{Volume in ml}} = \frac{1000 \text{ ml} \times 0.01 \text{ mole}}{100 \text{ ml}} = 0.1\text{M}$$

$$\text{Moles of NaCl in 10 mL} = \frac{\text{volume in ml} \times \text{mole}}{1000 \text{ ml}} = \frac{10 \text{ ml} \times 0.1 \text{ mole}}{1000 \text{ ml}} = 0.001\text{mole.}$$

Since the reaction ratio between silver nitrate and sodium chloride = 1:1, then the moles of silver nitrate reacted with sodium chloride was 0.001 mole.

$$\text{Therefore molarity of AgNO}_3 = \frac{0.001\text{mole} \times 1000 \text{ ml}}{9.325\text{ml}} = 0.107\text{M}$$

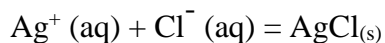
4.5.2 Concentration of chloride in Banisa borehole

Table 4.7 gives the titration data used in the calculation of chloride concentration.

Table 4.7: Banisa borehole sample titration using 0.107M AgNO₃

Burette reading	1	2	3	
Initial burette reading (mL)	0.00	4.70	9.40	
Final burette reading (mL)	0.09	4.80	9.50	
Volume of AgNO ₃ used	0.09	0.09	0.09	
Average volume of AgNO ₃ used	= 0.09 mL ± 0.01			

Reaction taking place during titration is shown in Scheme 4.2.



Scheme 4.2 Reaction of silver ion and chloride ion

$$\text{Moles of AgNO}_3 = \frac{M \times V}{1000} = (0.107 \times 0.098) / 1000 = 1.049 \times 10^{-5} \text{ mole} = \text{moles of Cl}^- \text{ in 25 mL}$$

of sample.

$$\text{Molarity of Cl}^- = \frac{\text{Mole} \times 1000 \text{ ml}}{\text{volume in ml}} = (0.00001049 \times 1000) / 25 = 0.0004197 \text{ M}$$

$$\text{Cl in mg/L} = (\text{molarity}) \times (\text{molecular weight of chloride}) \times (1000 \text{ mg/1g})$$

$$= (0.0004197 \text{ mole/l}) \times (35.5 \text{ g/ mole}) \times (1000 \text{ mg/1g})$$

$$= 14.9 \text{ mg/L}$$

$$\text{Equation is: Cl (mg/L)} = (\text{Molarity AgNO}_3) \times (\text{volume of AgNO}_3) \times (\text{M.w of Cl}) \times (40)$$

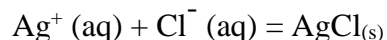
4.5.3 Concentration of chloride in Elwak borehole

Table 4.8 gives the titration data used in the calculation of chloride concentration.

Table 4.8 Elwak borehole sample titration using 0.107M AgNO₃

Burette reading	1	2	3	
Initial burette reading (mL)	0.00	4.70	9.40	
Final burette reading (mL)	0.79	5.49	10.19	
Volume of AgNO ₃ used	0.79	0.79	0.79	
Average volume of AgNO ₃ used	= 0.79 mL ± 0.02			

Reaction taking place during titration is given in scheme 4.2.



Scheme 4.2: Reaction of silver ion and chloride ion

Moles of AgNO₃ = $\frac{M \times V}{1000} = (0.107 \times 0.79) / 1000 = 8.45 \times 10^{-5}$ mole = moles of Cl⁻ in 25 mL of sample.

$$\text{Molarity of Cl} = \frac{\text{Mole} \times 1000 \text{ ml}}{\text{volume in ml}} = (0.0000845 \times 1000) / 25 = 0.00338 \text{M}$$

$$\begin{aligned} \text{Cl in mg/L} &= (\text{molarity}) \times (\text{molecular weight of chloride}) \times (1000 \text{mg/1g}) \\ &= (0.00338 \text{ mole/l}) \times (35.5 \text{ g/ mole}) \times (1000 \text{mg/1g}) \\ &= 119.9 \text{ mg/L} \end{aligned}$$

$$\text{Equation is: Cl (mg/L)} = (\text{Molarity AgNO}_3) \times (\text{volume of AgNO}_3) \times (\text{M.w of Cl}) \times (40)$$

4.5.4 Concentration of chloride in Takaba borehole

Table 4.9 gives the titration data used in the calculation of chloride concentration.

Table 4.9 Takaba borehole sample titration using 0.107M AgNO₃

Burette reading	1	2	3	
Initial burette reading (mL)	0.00	4.70	9.40	
Final burette reading (mL)	0.18	4.89	9.58	
Volume of AgNO ₃ used	0.18	0.19	0.18	
Average volume of AgNO ₃ used	= 0.18 mL ± 0.00			

Reaction taking place during titration is given in scheme 4.2.

$$\text{Moles of AgNO}_3 = \frac{M \times V}{1000} = (0.107 \times 0.184) / 1000 = 1.97 \times 10^{-5} \text{ mole} = \text{moles of Cl}^- \text{ in 25 mL}$$

of sample.

$$\text{Molarity of Cl}^- = \frac{\text{Mole} \times 1000 \text{ ml}}{\text{volume in ml}} = (0.0000197 \times 1000) / 25 = 0.000789 \text{ M}$$

$$\begin{aligned} \text{Cl in mg/L} &= (\text{molarity}) \times (\text{molecular weight of chloride}) \times (1000 \text{ mg/1g}) \\ &= (0.000789 \text{ mole/l}) \times (35.5 \text{ g/ mole}) \times (1000 \text{ mg/1g}) \\ &= 28 \text{ mg/L} \end{aligned}$$

$$\text{Equation is: Cl (mg/L)} = (\text{Molarity AgNO}_3) \times (\text{volume of AgNO}_3) \times (\text{M.w of Cl}) \times (40)$$

4.5.5 Concentration of chloride in Mandera borehole

Table 4.10 gives the titration data used in the calculation of chloride concentration.

Table 4.10 Mandera borehole sample titration using 0.107M AgNO₃

Burette reading	1	2	3	
Initial burette reading (mL)	0.00	4.70	9.40	
Final burette reading (mL)	0.15	4.85	9.55	
Volume of AgNO ₃ used	0.15	0.15	0.15	
Average volume of AgNO ₃ used	= 0.15 mL ± 0.00			

Reaction taking place during titration is given in scheme 4.2.

$$\text{Moles of AgNO}_3 = \frac{M \times V}{1000} = (0.107 \times 0.15) / 1000 = 1.61 \times 10^{-5} \text{ mole} = \text{moles of Cl}^- \text{ in 25 mL of}$$

sample.

$$\text{Molarity of Cl}^- = \frac{\text{Mole} \times 1000 \text{ ml}}{\text{volume in ml}} = (0.0000161 \times 1000) / 25 = 0.000645 \text{ M}$$

$$\begin{aligned} \text{Cl in mg/L} &= (\text{molarity}) \times (\text{molecular weight of chloride}) \times (1000 \text{ mg/1g}) \\ &= (0.000645 \text{ mole/l}) \times (35.5 \text{ g/ mole}) \times (1000 \text{ mg/1g}) \\ &= 22.9 \text{ mg/L} \end{aligned}$$

$$\text{Equation is: Cl (mg/L)} = (\text{Molarity AgNO}_3) \times (\text{volume of AgNO}_3) \times (\text{M.w of Cl}) \times (40)$$

4.5.6 Concentration of chloride in Shimbir Fatuma borehole

Table 4.11 gives the titration data used in the calculation of chloride concentration.

Table 4.11 ShimbirFatuma borehole sample titration using 0.107M AgNO₃

Burette reading	1	2	3	
Initial burette reading (mL)	0.00	4.70	9.40	
Final burette reading (mL)	0.05	4.75	9.45	
Volume of AgNO ₃ used	0.05	0.05	0.05	
Average volume of AgNO ₃ used	= 0.05 mL ± 0.00			

Reaction taking place during titration is shown in scheme 4.2.

Moles of AgNO₃ = $\frac{M \times V}{1000} = (0.107 \times 0.05) / 1000 = 5.63 \times 10^{-6}$ mole = moles of Cl⁻ in 25 mL of sample.

Molarity of Cl = $\frac{\text{Mole} \times 1000 \text{ ml}}{\text{volume in ml}} = (0.00000563 \times 1000) / 25 = 0.000225 \text{ M}$

Cl in mg/L = (molarity) × (molecular weight of chloride) × (1000mg/1g)
 = (0.000225 mole/l) × (35.5 g/ mole) × (1000mg/1g)
 = 7.99 mg/L

Equation is: Cl (mg/L) = (Molarity AgNO₃) × (volume of AgNO₃) × (M.w of Cl) × (40)

A summary of the content of chloride in borehole waters is given in Table 4.12.

Table 4.12 Content of chloride in water samples

BOREHOLE	mg/L
Banisa	14.99±1.11
Takaba	28.00 ±2.31
Elwak	119.90±3.11
Mandera	22.99±1.40
Shimbir Fatuma	7.99±1.80

Fig 4.6 is a graphic data of chloride content in the five boreholes.

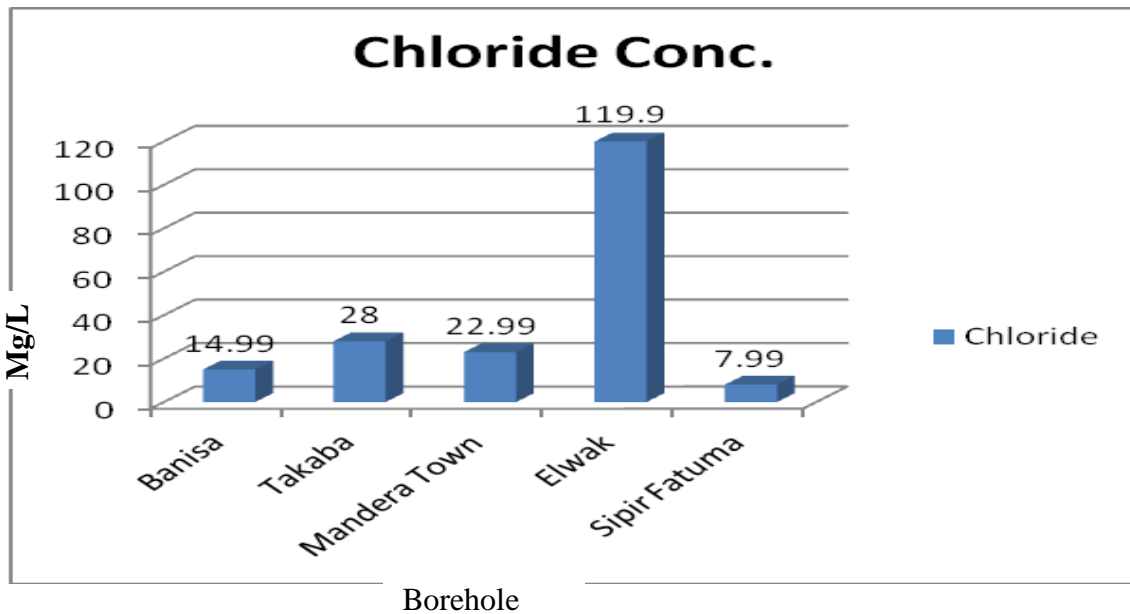


Figure 4.6 The level of chloride ion (mg/L) in water samples

4.6 Nitrate

The value of nitrates had a range of 0.316mg/L – 2.86mg/L. The maximum value of 2.86 mg/L was recorded in ShimbirFatuma and the lowest of 0.316 mg/L in Banisa borehole. These values are within the permissible limit as prescribed by WHO (50 mg/L) and NEMA (10 mg/L) (Table 4.13) (Appendixes 1-5).

Table 4.13 Nitrate content values (mg/L) in borehole water samples

BOREHOLE	Concentration mg/L $x = (y - 0.0019) / 0.0158$	y=Absorbance
Banisa	0.316	0.007
Takaba	0.968	0.017
Elwak	1.898	0.032
Mandera	1.672	0.028
Shimbir Fatuma	2.860	0.047

Table 4.14 shows the absorbance values for nitrate standards

Table 4.14 Absorbance values for nitrate standards

S/NO:	Concentration (ppm)	Absorbance
1	1.000	0.014
2	2.000	0.029
3	3.000	0.046
4	4.000	0.061
5	5.000	0.077
6	6.000	0.093
7	7.000	0.109
8	8.000	0.125
9	9.000	0.140
10	10.000	1.156

Fig 4.7 shows absorbance versus concentration for nitrate standards.

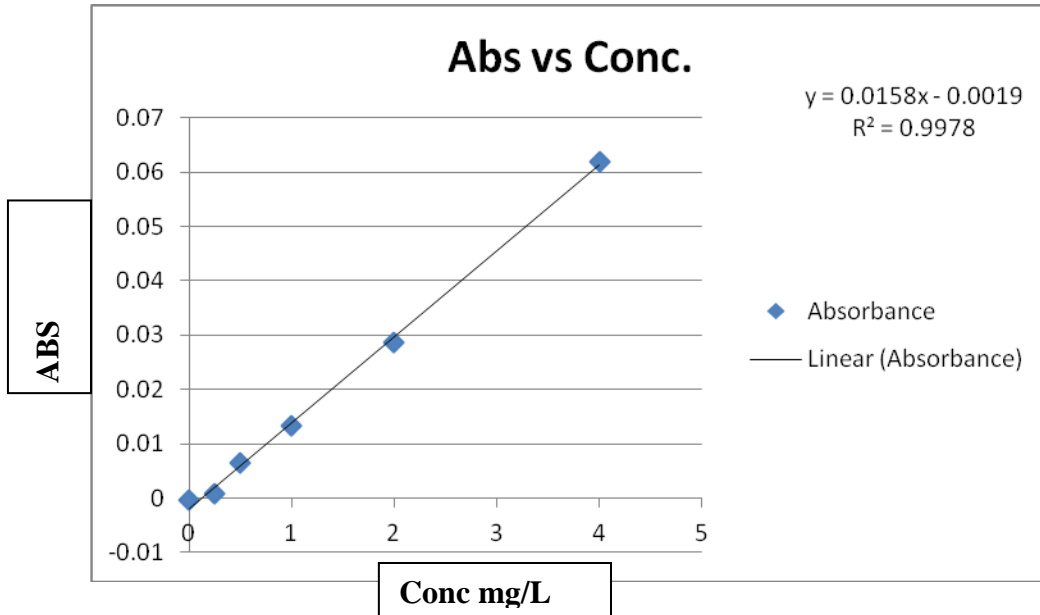


Figure 4.7 Calibration graph for nitrate

Fig 4.8 shows the graph data of concentration of nitrate in various boreholes.

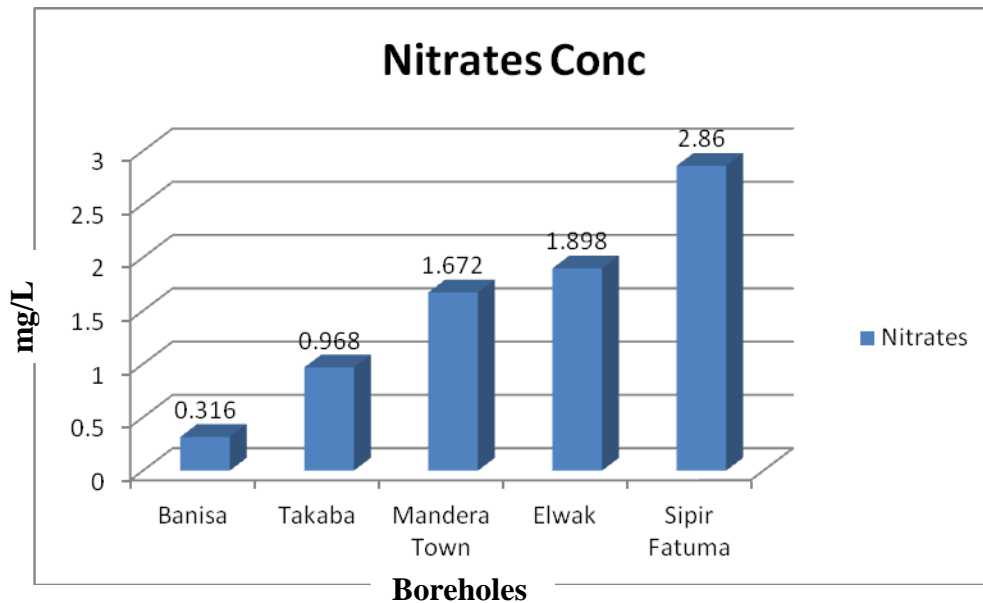


Figure 4.8 The level of nitrate ion (mg/L) in water samples

The level of nitrates increased as one moved from Banisa, Takaba, Mandera Town, Elwak and ShimbirFatuma. There were agricultural activities around ShimbirFatuma and

Elwak which could possibly explain the enhanced nitrate content which originated from fertilizer use. Other factors included municipal and industrial waste water, refuse dumps, septic tanks and private sewage disposal systems. There were no similar activities around Banisa and Takaba.

4.7 Ammonium - NH_4^+

The values of ammonium ions were found to be in the range 0-0.66 mg/L which was all within the acceptable NEMA limits of 0.50 mg/L (Table 4.16). There is no WHO guideline value. Because of its solubility ammonium may penetrate deeper into soils and eventually reach groundwater. In some soils part of the ammonium may be converted to nitrites and nitrates before or after it reaches groundwater. Table 4.15 shows the absorbance value for ammonium standards.

Table 4.15 Absorbance values for ammonium standards

S/NO:	Concentration (ppm)	Absorbance
1	0.130	-0.044
2	0.260	-0.023
3	0.390	0.005
4	0.520	-0.014
5	0.640	0.030
6	0.770	0.049
7	0.900	0.067
8	1.030	0.085
9	1.160	0.103
10	1.290	0.122

Data in Table 4.15 was used to plot Fig 4.9.

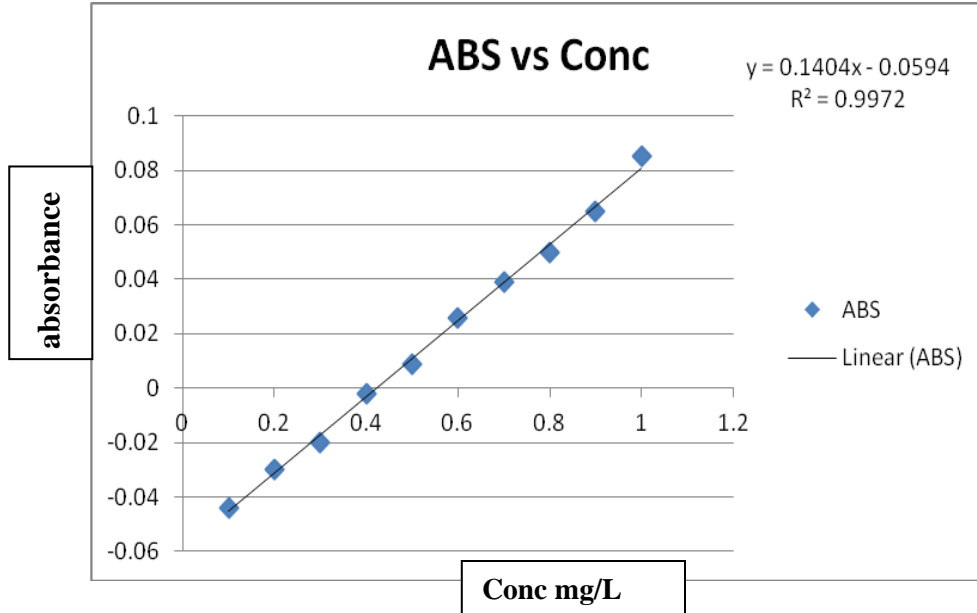


Figure 4.9 Calibration graph for ammonium

Data for borehole samples are given in Table 4.16. The equation in Fig. 4.9 ($y=0.1404x-0.0594$) was used to calculate the concentration of ammonium in the samples (Appendixes 1-5).

Table 4.16 Ammonium absorbance values for borehole waters

Borehole	Concentration (ppm) $x = (y + 0.0594) / 0.1404$	Absorbance=y
Banisa	0.6600	0.0333
Takaba	0.0600	-0.0510
Shimbir Fatuma	0.0000	-0.0594
Mandera Town	0.0000	-0.0594
Elwak	0.0000	-0.0594

Table 4.16 data was used to draw Fig.4.10.

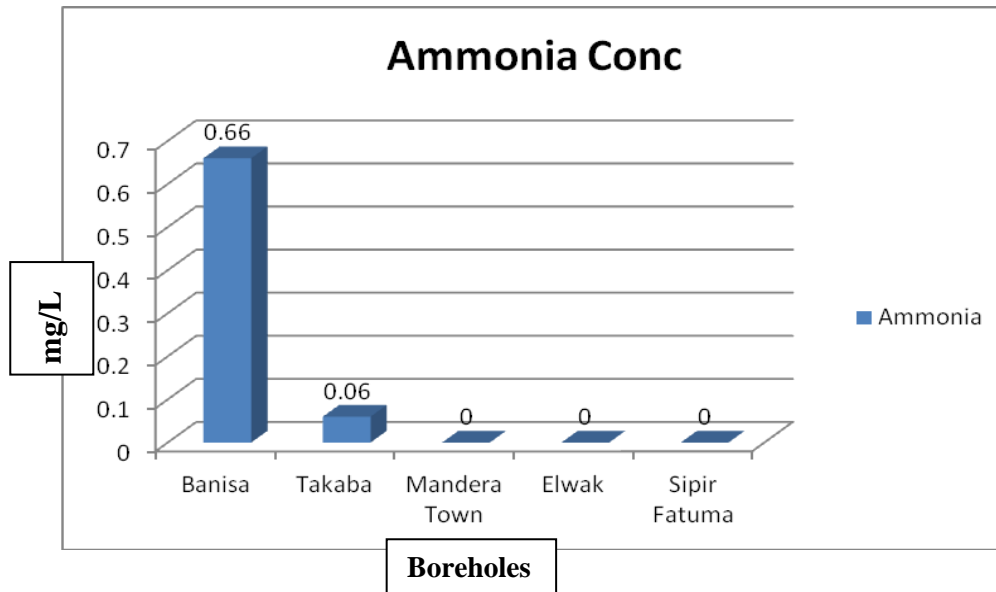


Figure 4.10 The level of ammonium (mg/L) in water samples

Banisa had enhanced ammonium content possibly due to increased livestock activities in the area as compared to the other places. Livestock husbandry will increase ammonium discharge into the environment.

4.8 Sodium

The concentration of sodium was observed to be within the range of 11.2 mg/L – 46.4 mg/L for all samples. There is no guideline value for sodium. Table 4.17 shows the emission values for sodium and potassium standards.

Table 4.17 Emission values for sodium and potassium standards

S/NO:	Concentration (ppm)	Emission Sodium	Emission Potassium
1	0.5	006	005
2	1.0	011	010
3	2.0	022	023
4	4.0	043	041
5	6.0	067	063
6	8.0	084	083
7	10.0	103	100

The data in Table 4.17 was used to tabulate Figs 4.11 and 4.12. The straight line equations were used in calculating the concentration of borehole waters of sodium and potassium.

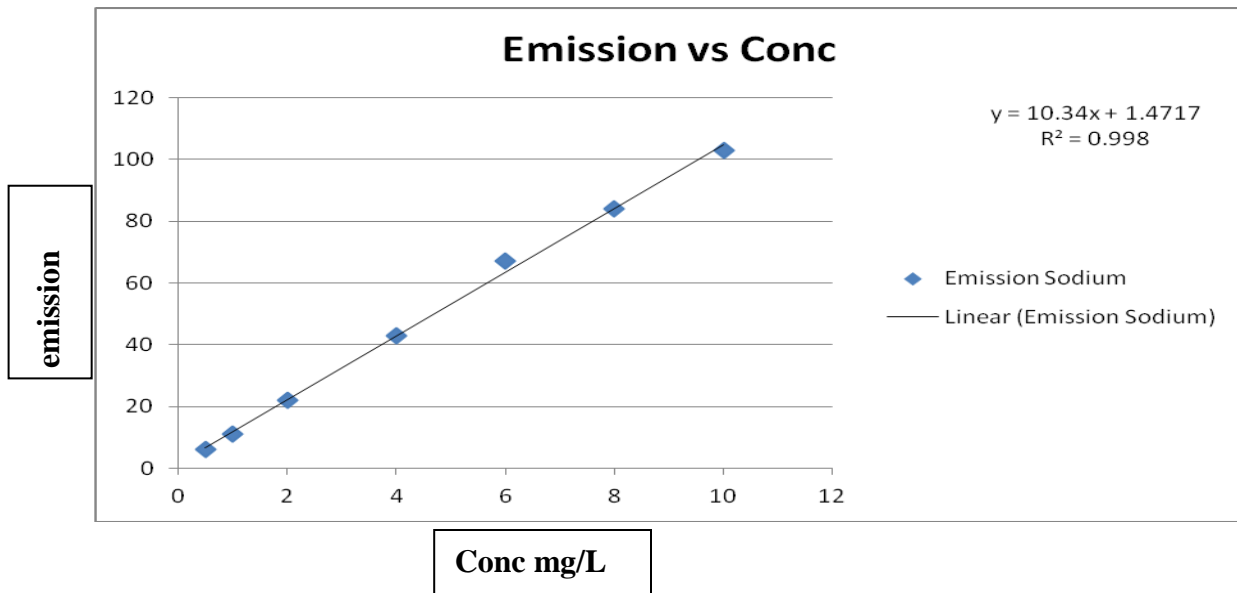


Figure 4.11 A linear calibration graph for sodium

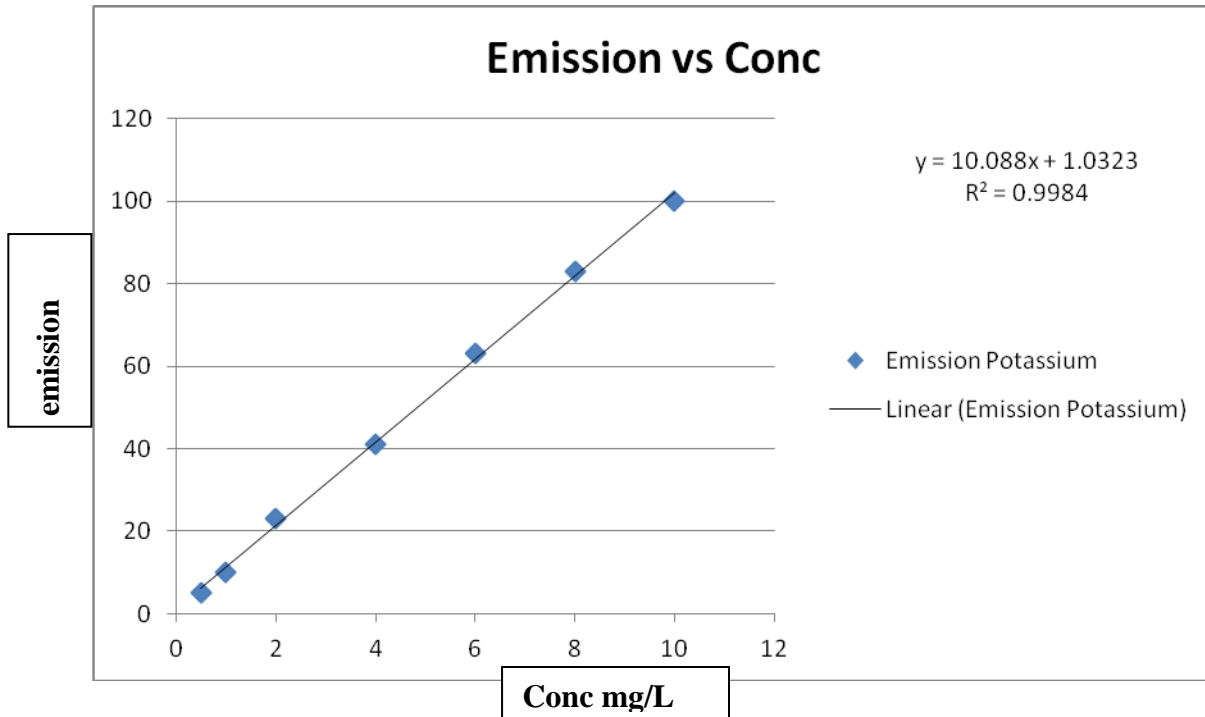


Figure 4.12 A linear Calibration graph for potassium

Table 4.18 shows the emission values for sodium in the borehole samples. The emission value of the samples was used to calculate the concentration values using equation in Fig. 4.11 (Appendixes 1-5).

Table 4.18 Sodium concentration (mg/L) in borehole water samples

BOREHOLE	$x = (y - 1.4717) / 10.34 \text{ mg/L}$	Emission, $y = 10.34x + 1.4717$
Banisa	11.20	117.27
Takaba	22.20	231.02
Elwak	46.40	481.25
Mandera Town	18.40	191.70
Shimbir Fatuma	35.50	368.54

The range of sodium was 18.4-46.4 mg/L in the samples. Elwak gave the highest concentration. Table 4.18 was used to draw Fig. 4.13.

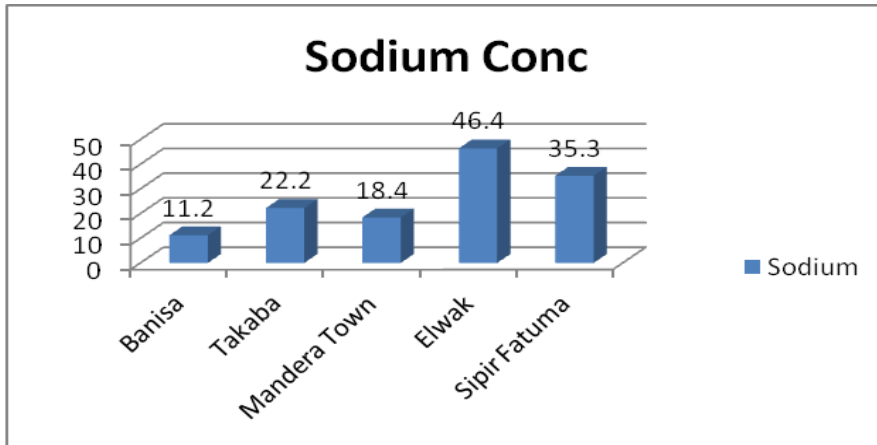


Fig 4.13 The level of sodium ion (mg/L) in water samples

The concentration of potassium was observed to be within the range of 4.6 mg/L – 101.4 mg/L). Elwak borehole recorded the highest value of 101.4 mg/L and Takaba borehole recorded 4.6 mg/L (Table 4.19). Elwak possibly had enhanced amount of soluble sodium containing ores. There is no guideline value set by WHO and NEMA. Table 4.19 gives data of emission versus concentration of potassium in borehole samples. The emission data was used to calculate the concentration of potassium in the samples using equation in Fig. 4.12 (Appendixes 1-5).

Table 4.19 Potassium concentration (mg/L) in borehole water samples

BOREHOLE	$x = (y - 1.0323) / 10.088$ mg/L	Emission, $y = (10.088x + 1.0323)$
Banisa	17.70	179.59
Takaba	4.60	47.44
Elwak	101.40	1023.90
Mandera Town	4.70	48.44
Shimbir Fatuma	12.30	125.10

Table 4.19 data was used to draw Fig. 4.14.

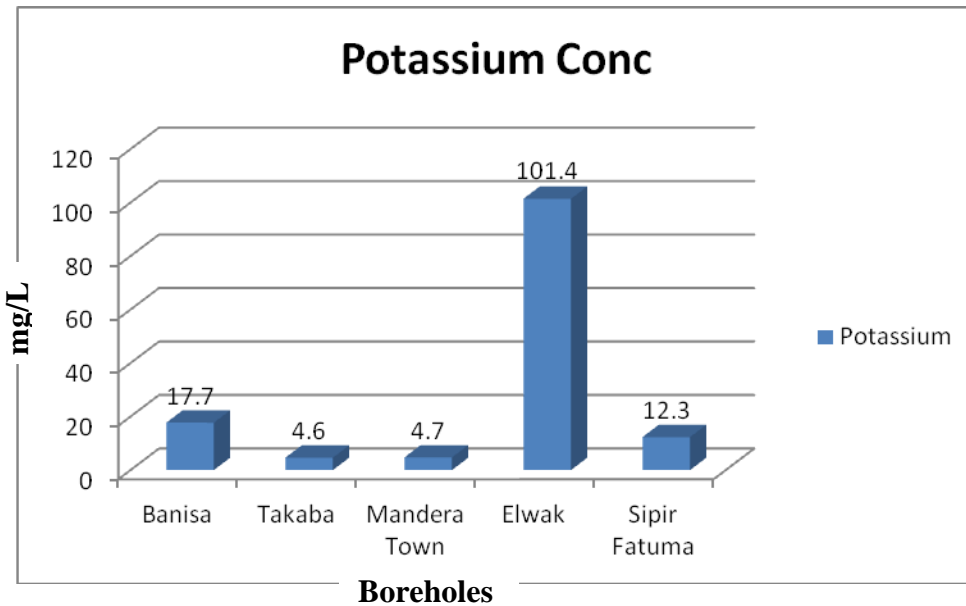


Figure 4.14 The level of potassium ion (mg/L) in water samples

Elwak possibly had enhanced amount of soluble potassium containing ores which elevated its content in the borehole.

4.9 Heavy Metals

4.9.1 Lead

Lead content in the water samples were below the detection of the instrument which was 0.25 ppm. This indicated that the water samples did not contain detectable lead showing that its concentration was below the NEMA and WHO limits of 0.05mg/L, 0.01mg/L respectively for domestic water. The lead values obtained were further verified using total reflection X-ray Fluorescence (TXRF) which gave values less than 0.01mg/L.

Table 4.20 shows the absorbance versus concentration for lead standards.

Table 4.20 Absorbance versus concentration of lead standards

S/NO:	Concentration (ppm)	Absorbance
1	0.00	-0.0003
2	0.25	0.0008
3	0.50	0.0065
4	1.00	0.0134
5	2.00	0.0286
6	4.00	0.0620

Data in Table 4.20 was used to plot the calibration graph in Fig. 4.15

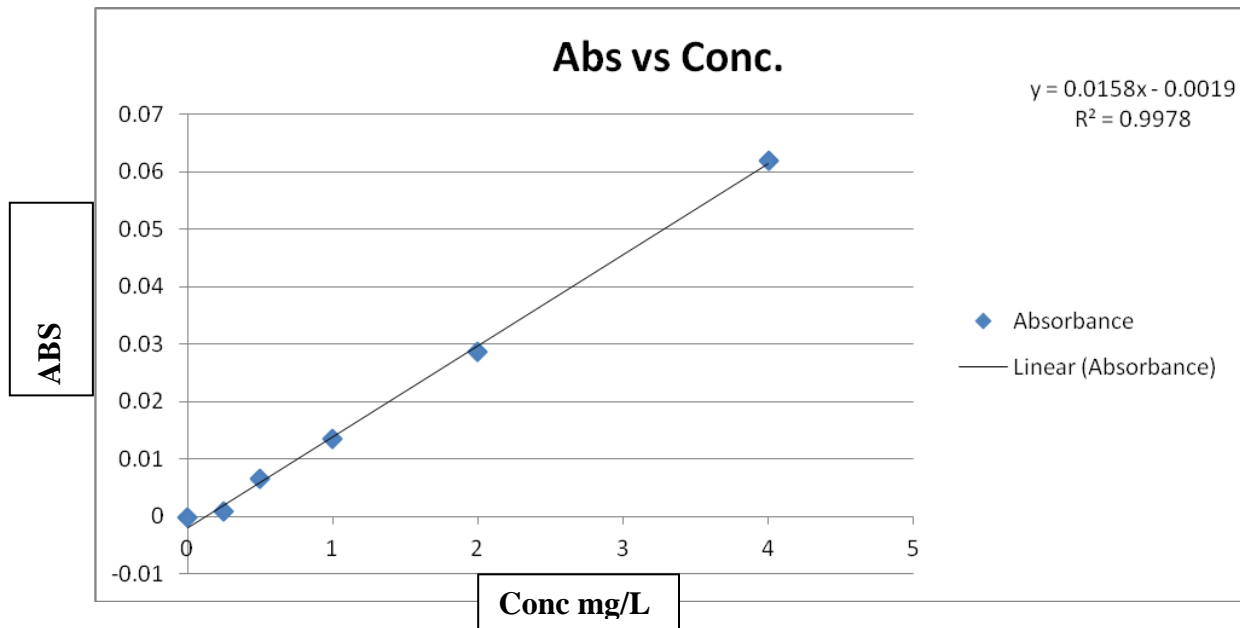


Figure 4.15: Calibration graph for lead

The equation $y = 0.0158x - 0.0019$ in Fig 4.15 was used to calculate the concentration of lead in the samples in Table 4.21. Table 4.21 gives concentration versus absorbance of borehole samples (Appendixes 1-5).

Table 4.21: Absorbance versus concentration of lead in borehole waters

Borehole	Concentration, $(y+0.0019)/0.0158$ mg/L	Absorbance, $y = (0.0158x - 0.0019)$
Banisa	0	-0.0019
Takaba	0	-0.0019
Mandera Town	0	-0.0019
Elwak	0	-0.0019
Shimbir Fatuma	0	-0.0019

4.9.2 Zinc

Zinc values for the water samples were below the detection of the instrument which was 0.1 ppm. This indicates that the water samples did not contain detectable zinc showing that its concentration was below the NEMA and WHO limits. Table 4.22 shows the absorbance versus concentration for zinc standards

Table 4.22 Absorbance values for zinc standards

S/NO:	Concentration mg/L	Absorbance
1	0.0	0.0000
2	0.1	0.0473
3	0.2	0.0923
4	0.4	0.1698
5	0.6	0.2423
6	1.0	0.3702

Table 4.22 was used to draw the calibration graph in Fig 4.16.

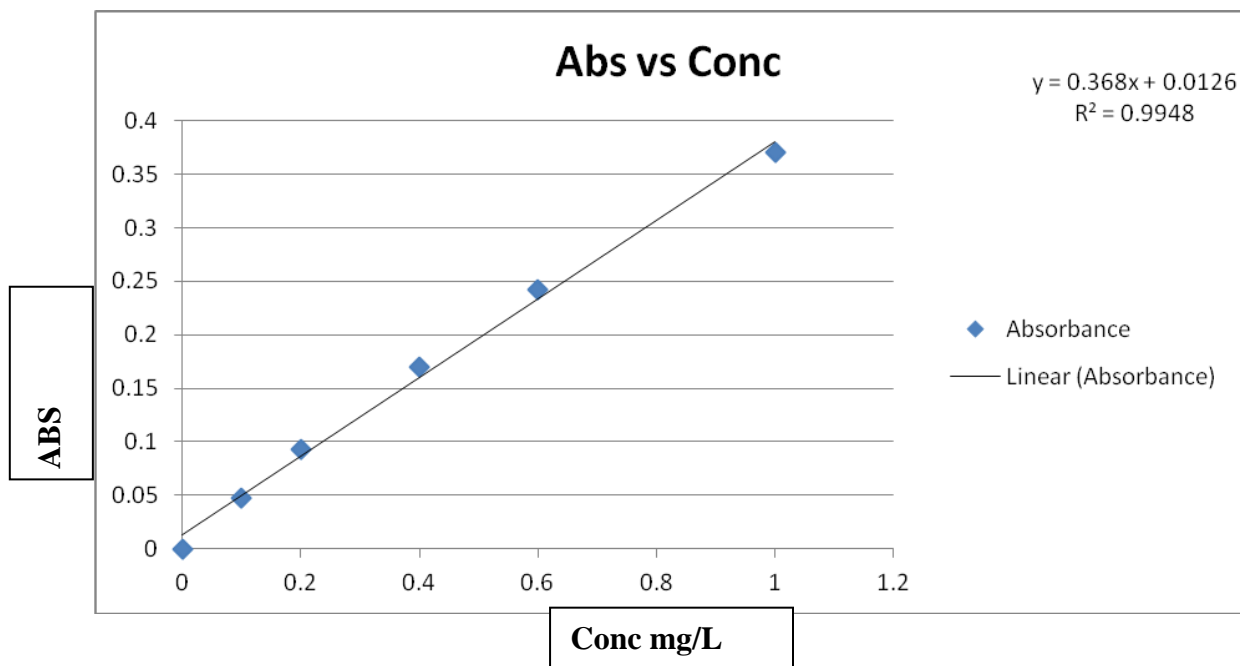


Figure 4.16: Calibration graph for zinc

Table 4.23 shows the data for concentration versus absorbance of zinc in borehole waters (Appendixes 1-5).

Table 4.23 Absorbance versus concentration of zinc in borehole waters

Borehole	Concentration, mg/L	Absorbance, $y = (0.368x + 0.0126)$
Banisa	0.0774	0.041
Takaba	0.0600	0.035
Mandera Town	0.0570	0.034
Elwak	0.1890	0.082
Shimbir Fatuma	0.0670	0.037

The concentration of zinc in the boreholes ranged from 0.057-0.189 mg/L. This is depicted in Fig. 4.17.

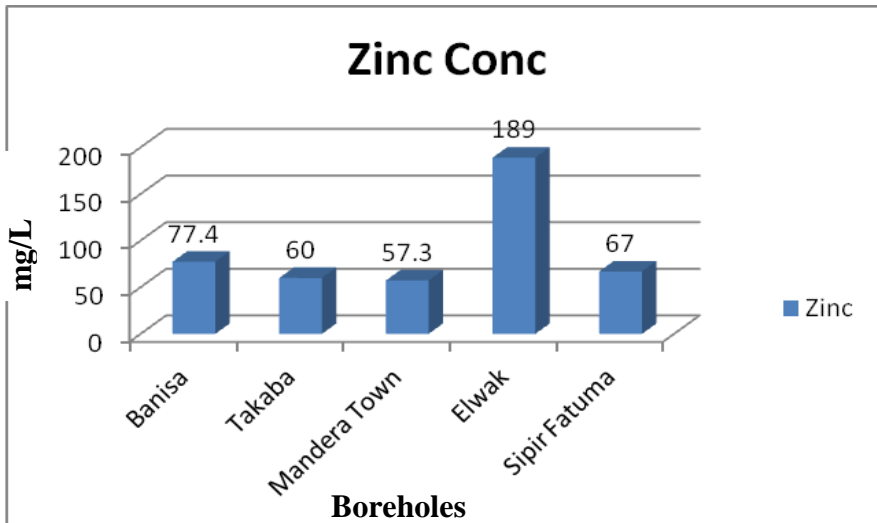


Fig 4.17 The level of Zinc ion ($\text{mg/L} \times 10^{-3}$) in water samples

Lwak had the highest zinc ion concentration which was below the WHO and NEMA guideline values.

4.10 Other metals

Total Reflectance X-ray fluorescence was used to get the content of the other metals and the results are tabulated in Table 4.24.

Table 4.24: Concentration of elements in ppb ($\mu\text{g/l}$) for the boreholes

Elements	Banisa	Takaba	Mandera Town	Elwak	ShimbirFatuma
Calcium (Ca)	16300 \pm 1480	18517 \pm 1194	78655 \pm 1583	267594 \pm 13013	35445 \pm 1350
Titanium (Ti)	105 \pm 10	<50	<50	<50	<50
Vanadium (V)	<30	<30	<30	122 \pm 12	<30
Chromium (Cr)	<30	<30	<30	<30	<30
Manganese (Mn)	45.0 \pm 4.1	<20	<20	<20	<20
Iron (Fe)	1533 \pm 119	259 \pm 19	133 \pm 7	75.0 \pm 7.1	320 \pm 9
Nickel (Ni)	<20	<20	<20	<20	<20
Copper (Cu)	<20	<20	<20	<20	<20
Arsenic (As)	<20	<20	<20	<20	<20
Selenium (Se)	<20	<20	<20	<20	<20
Mercury (Hg)	<30	<30	<30	<30	<30
Lead (Pb)	<10	<10	<10	<10	<10

Calcium ion was in the largest amount possibly due to the presence of calcium carbonate in the rock strata. Elwak seem to have had more of these in its rocks as compared to the other boreholes.

4.11 Bacteriological Analysis

4.11.1 Escherichia Coli

Laboratory results showed that there was no Escherichia Coli detected in sampled water hence in line with the required standards of nil/100mL. However coliforms were presents.

4.11.2 Confirmation test

Table 4.25 gives confirmatory tests for *E. Coli* in water samples.

Table 4.25: Confirmatory Tests Result for *E.coli* in water samples

Water sources	Colony colours	Organism(s) present
Banisa	No Color Change	No. <i>E.coli</i>
Shimbir Fatuma	No Colour Change	No. <i>E.coli</i>
Takaba	No colour Change	No. <i>E.coli</i>
Mandera Town	No Colour Change	No <i>E.coli</i>
Elwak	No Colour Change	No <i>E.coli</i>

The colonies were then gram stained. Pink and purple colors were identified as gram negative and positive respectively. These are shown in Figs 4.18, 4.19, 4.20, 4.21 and 4.22 (Appendixes 1-5).

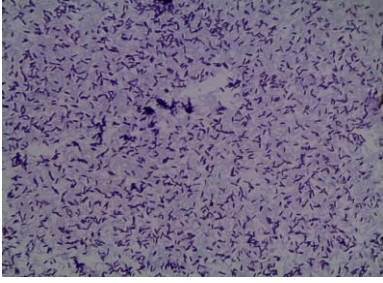


Fig 4.18: Banisa short rods coliforms

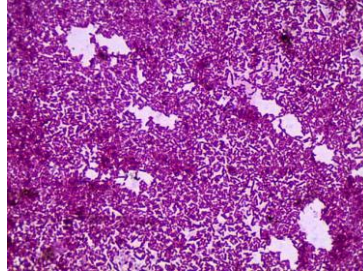


Fig 4.19 Shimbir Fatuma short rods coliforms

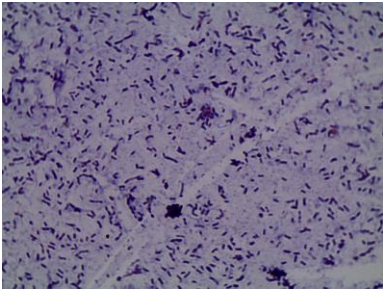


Fig 4.20 : Takaba short rods coliforms

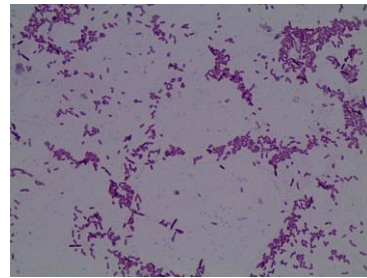


Fig 4.21: Mandera Town short rods coliforms

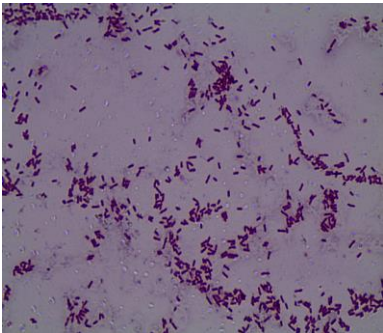


Fig 4.22 Elwak town short rods coliforms



Figure 4.23: Quantitative analysis for *E. coli* in all towns

The results of *E. coli* content are shown graphically in Fig 4.24.

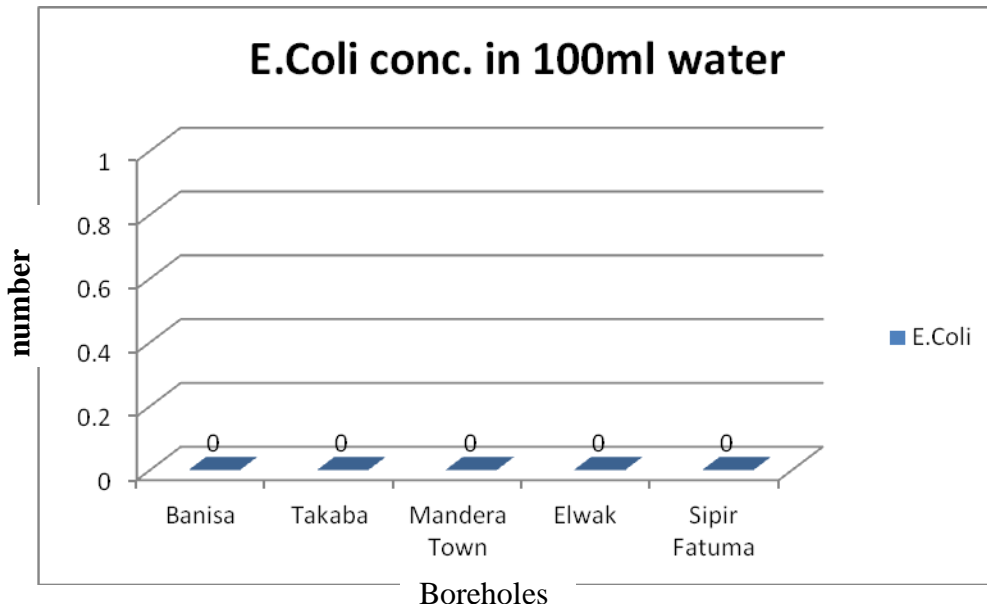


Figure 4.24: The level of *E.coli* (counts/100mL) in water samples

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The pH values in all the five boreholes were within the WHO and NEMA guideline value (6.5-8.5) except Banisa, Mandera Town and Shimbir Fatuma. Electrical conductivity and total dissolved solids had all values within the guideline except Elwak. The values for fluoride, nitrate, zinc, lead and *E-coli* were all within the WHO and NEMA guideline values.

Chloride values for all boreholes were all within WHO (250 mg/L). There is no NEMA guideline. Ammonium ions in all samples were within NEMA guideline (0.5 mg/L). There is no corresponding WHO guideline value. Sodium and potassium ions had a range of 11.2-46.4 mg/L and 4.6-101.4 mg/L respectively. However, there is no WHO and NEMA guideline values.

E.coli was not detected in all the boreholes while Coliforms were present in all. Banisa, Mandera Town, and Shimbir Fatuma had all parameters meeting the standards except for pH that was found to be lower than 6.5. Takaba and Elwak had all parameters within guideline values except electrical conductivity and total dissolved solids.

5.2 Recommendations

This study, therefore recommends the following:

1. Introduce relevant drinking water treatment and conditioning techniques to increase the pH of Banisa, Mandera and Shimbir Fatuma borehole waters.
2. Further studies should be carried out to identify coliforms found in water to establish their potential risk to the consumers.

3. Appropriate methods should be devised in reducing total dissolved solids in Takaba and Elwak boreholes.
4. Studies should be undertaken to assess the entire boreholes in Mandera County.
5. Further studies on cadmium and copper content should be done.

REFERENCES

- APHA**, (1992) Standard Methods for the Examination of Water and Waste Water. 18th ed. American Public Health Association, Washington, DC, U.S.A.
- Babcock**, R. W. and Walton, R. (2008). World Environmental and Water Resources Congress, Honolulu, HI.
- Beckoff**, B., Fliegau, R., Rolbe, M., Muller, M., Weser, J. and Ul, G. (2007). Free total reflection X-ray fluorescence analysis of semiconductor surfaces with synchrotron radiation, *Anal. Chem.*, **79** (20): 7873-7882.
- Bouwer**, E.J. and Crowe, P.B. (1988). Biological Processes In Drinking Water Treatment. *J. Am. Water Works Assoc.*, **80**(9): 82-93.
- Broekaert**, J.A.C.(1998). Analytical Atomic Spectrometry with Flames and Plasmas, 3rd Edition, Wiley-VCH, Weinheim, Germany.
- Bruch**, C. (2005). Public Participation in the Governance of International Freshwater Resources.
- Cohen**, J.M. (1960). Taste Threshold Concentrations Of Metals In Drinking Water. *Journal of the American Water Works Association*, **52**: 660.
- Chatwal**, G.R. and Anand, S.(2002). Instrumental Methods of Chemical Analysis. 5th Edition, Himalaya Publishing House, New Delhi, India.
- Davis**, R. K., (1968). The Range of Choice in Water Management: A Study of Dissolved Oxygen in the Potomac Estuary, 2nd Edition, Elsevier Science Publishers, New York, U.S.A.
- Dean**, J. A. and Rains, T.C.(1971). Flame Emission and Atomic Absorption Spectrometry Volumes 1 & 2, Marcel Dekker Inc., New York, U.S.A.

- Drelich, J.** (2011). *Water in Mineral Processing: Proceedings of the first International Symposium Engle. Wood Colo: Society for Mining, Metallurgy, and Exploration.*
- Elinder, C.G, Friberg, L., Nordberg, G.F. and Vouk, V.B.**(2014) eds. *Handbook on the toxicology of metals, 2nd ed., Elsevier Science Publishers, Amsterdam, Holland: 664-679.*
- Flame Photometer** (2009). *Operating and Service Manual, Models PFP7 and PFP7/C.*
- Garrett, L.,** (1994). *The Coming plague: Newly Emerging Diseases in a World out of Balance. Cambridge university publishers, New York, U.S.A.*
- Gleick, P. H.,** (1993) .*Water in Crisis: A Guide to the World's Freshwater Resources, Oxford University Press, London, United Kingdom.*
- Gregory, R.** (1990). *Galvanic Corrosion of Lead Solder in Copper Pipework. Journal of the Institute of Water and Environmental Management, 4(2): 112.*
- Hargis, L.G.** (1988). *Analytical Chemistry: Principles and Techniques; Prentice Hall: Englewood Cliffs, NJ, U.S.A., 451–463.*
- Heritage, J. and Evans, E. G.** (1999). *Microbiology in Action. Cambridge University Press, Cambridge, United Kingdom.*
- Hirsch, E. H.** (1980). *Stress in Porous Thin Films through Absorption of Polar Molecules. Ft., Technical Report.*
- Holte, A.** (1993). *Diameter Distribution Functions for Even-aged (Picea abies) stands Diameter fordelingsfunksjoner for ensaldrede bestand av gran (picea abies). AAS: Norwegian Forest Research Institute.*

- Jaff**, H.H. and **Urchin**, M.(1962). Theory and Applications of Ultraviolet Spectroscopy, John Wiley and Sons Inc., New York, U.S.A.
- Kalsi**, P.S.(2004). Spectroscopy of Organic Compounds, 6th Edition, New Age International Publishers Ltd., New Delhi, India.
- Katko**, T. S. (2013). Water Services Management and Governance Lessons for a Sustainable Future, London.
- Kaur**, H. (2008). Analytical Chemistry. Meerut, IND: Pragati Prakashan. Retrieved from <http://www.ebrary.com>
- Kenkel**, J. (1994). Analytical Chemistry for Technicians, 2nd ed., Lewis Boca Raton, FL, 289–297.
- Klockenkämper**, R., **Knoth** J., **Prange**, A. and **Schwenke**, H.(1992). Total reflection X-ray fluorescence, Anal. Chem., **64**, 1115A-1123A.
- Klockenkämper**, R. (1997) Total-Reflection X-Ray Fluorescence Analysis, John Wiley & Sons.
- Leopold**, L. B. and **Davis**, K. S. (1966). Water. New York: Time, Inc.
- L’vov**, B.V. (2005). Fifty years of atomic absorption spectrometry. J. Anal. Chem., **60**: 382-392.
- McGlade**, J. M. (2012). Measuring Water use in a Green Economy. United Nations Environment Programme, Nairobi, Kenya.

- Misra, P.** and Dubinskii, M., (2002). Ultraviolet Spectroscopy and UV Lasers. New York, Marcel Dekker. ISBN 0-8247-0668-4.
- Nriagu, J.O.**(1980). Zinc in the environment. Part I, Ecological cycling. John Wiley and Sons Ltd., New York, U.S.A.
- NSW,** (2003). Planning and evaluating Area Assistance Scheme Projects: A Resource kit for community project officers.
- Pavia, D.L., Lampmom, G.M. and Kriz, G.S.** (1996). Introduction to Spectroscopy, John Wiley and Sons Ltd., New York, U.S.A.
- Robbins, P.** (2007). Encyclopedia of Environment and Society. Thousand Oaks: Sage Publications, Thousand Oaks, U.S.A.
- Reinhold K. and Alex von B.**(2015). Total-Reflection X-Ray Fluorescence Analysis and Related Methods, Wiley, 2nd Edition, 79-200, ISBN: 978-1-118-46027-6.
- Schwartz, M. C.** (1935). Dissolved Oxygen in Boiler Feedwater Section One. The Determination of Dissolved Oxygen. Louisiana State University Press, Baton Rouge, U.S.A.
- Schilling, K.E.** (2002). Occurrence and Distribution of Ammonium in Iowa Groundwater. *Water Environ. Res.*, **74**(2): 177-186.
- Self, J.R. and Waskom, R.M.** (2008). Nitrates in drinking water, Colorado State University Crop Series no. 0.517.
- Skoog, D.,** (2007) Principles of Instrumental Analysis, 6th Ed., Thomson Brooks/Cole, Canada.
- Soltanpour, P.N., Broner, I. and Follett, R.H.** (1999). Nitrogen and Irrigation Management

- Stanton, T.L** (1992). Nitrate poisoning, Colorado State University Crop Series no. 1.610.
- Scheiner, D.** (1975). Determination of Ammonia and Kjeldahl nitrogen by Indophenol method, *Water Research*, **10**(1): 31-36.
- Terrio, P. J.** (1995). Water Quality Assessment of the Upper Illinois River Basin in Illinois Indiana, and Wisconsin: nutrients, dissolved oxygen, and Feca –Indicator bacteria in surface water, April 1987 through August 1990. Washington, D. C: U.S. Dept of the Interior, U.S. Geological Survey.
- UNEP** (1990). GEMS/Water data summary 1985—1987. Burlington, Ontario, Canada Centre for Inland Waters; United Nations Environment Programme, Global Environment Monitoring System, GEMS/Water Programme Office.
- USEPA** (1987). Estimated National Occurrence and Exposure to Nitrate and Nitrite in Public Drinking Water Supplies. Washington, DC, United States Environmental Protection Agency, Office of Drinking Water.
- UN** (United Nations) (2015). The UN World Development Report
- Waldron, M. C. and Wiley, J. B.,** (1996). Water Quality and Processes Affecting Dissolved Oxygen concentrations in the Blackwater River, Canaan Valley, West Virginia. Charleston, W. Va: U.S. Dept of Interior, U.S. Geological Survey.
- Wesson, L.G.** (1969). Physiology of the Human Kidney. Grune and Stratton, New York, U.S.A.: 591.
- WHO/ UNICEF,** (2010). WHO/UNICEF Joint Monitoring Programme (JMP) for water.

- WHO** (1996) Guidelines for drinking water quality, 2nd ed. Vol. 2. Health criteria and other supporting information, Geneva, Switzerland.
- WHO**, (2003). Background Document for Preparation of WHO Guidelines for Drinking water quality, Geneva, Switzerland.
- WHO**, (2004). Fluoride in Drinking Water: Background Document for Development of WHO Guidelines for Drinking Water Quality p.2.
- WHO**, (2009). Potassium in Drinking Water: Background Document for Development of WHO Guidelines for Drinking Water Quality.
- WHO** (2011). Calcium in Drinking Water: Background Document for Development of WHO Guidelines for Drinking Water Quality
- Yang**, J. E.(1998). A Simple Spectrophotometric Determination of Nitrate in Water, Resin and Soil Extracts. *Soil Science Society of America Journal* **62** (4): 1108-1115.
- Zoeteman**, B.C.J. (1980). Sensory Assessment of Water Quality. Pergamon Press , New York, U.S.A.
- Zacarias**, I. (2001). Determination of the Taste Threshold of Copper in Water. *Chemical Senses*, **26**(1):85–89.

APPENDIX 1

Statistical Analysis of Banisa Borehole

Parameters	Banisa	WHO	NEMA
pH	5.1	6.5-8.5	6.5-8.5
Electrical conductivity	840 $\mu\text{S}/\text{cm}$	2000 $\mu\text{S}/\text{cm}$	2400 $\mu\text{S}/\text{cm}$
Total dissolved solids	520 mg/L	1000 mg/L	1200 mg/L
Fluoride	0 mg/L	1.5 mg/L	1.5 mg/L
Chloride	14.99 mg/L	250 mg/L	No guideline value
Ammonium-NH ₄ ⁺	0.66 mg/L	No guideline value	0.5 mg/L
Nitrate NO ₃ ⁻	0.316 mg/L	50 mg/L	10 mg/L
Sodium	34.6 mg/L	No guideline value	No guideline value
Potassium	17.7 mg/L	No guideline value	No guideline value
Lead	Not detected	0.01 mg/L	0.05 mg/L
Zinc	77.4 $\mu\text{g}/\text{l}$	3mg/L	1.5 mg/L
<i>E.coli</i>	Nil/100	Nil/100	Nil/100

APPENDIX 2

Statistical Analysis of Takaba Borehole

Parameters	Takaba	WHO	NEMA
pH	7.13	6.5-8.5	6.5-8.5
Electrical conductivity	1654 $\mu\text{S/cm}$	2000 $\mu\text{S/cm}$	2400 $\mu\text{S/cm}$
Total dissolved solids	1025 mg/L	1000 mg/L	1200 mg/L
Fluoride	0.35 mg/L	1.5 mg/L	1.5 mg/L
Chloride	28 mg/L	250 mg/L	No guideline value
Ammonium-NH ₄ ⁺	0.06 mg/L	No guideline value	0.5 mg/L
Nitrate NO ₃ ⁻	0.968 mg/L	50 mg/L	10 mg/L
Sodium	22.2 mg/L	No guideline value	No guideline value
Potassium	4.6 mg/L	No guideline value	No guideline value
Lead	Not detected	0.01 mg/L	0.05 mg/L
Zinc	60.0 $\mu\text{g/l}$	3mg/L	1.5 mg/L
<i>E.coli</i>	Nil/100	Nil/100	Nil/100

APPENDIX 3

Statistical Analysis of Mandera Town Borehole

Parameters	Mandera	WHO	NEMA
pH	5.3	6.5-8.5	6.5-8.5
Electrical conductivity	797 μ S/cm	2000 μ S/cm	2400 μ S/cm
Total dissolved solids	494 mg/L	1000 mg/L	1200 mg/L
Fluoride	0.2 mg/L	1.5 mg/L	1.5 mg/L
Chloride	22.99 mg/L	250 mg/L	No guideline value
Ammonium-NH ₄ ⁺	0.0 mg/L	No guideline value	0.5 mg/L
Nitrate NO ₃ ⁻	1.672 mg/L	50 mg/L	10 mg/L
Sodium	18.4 mg/L	No guideline value	No guideline value
Potassium	4.7 mg/L	No guideline value	No guideline value
Lead	Not detected	0.01 mg/L	0.05 mg/L
Zinc	57.3 μ g/l	3mg/L	1.5 mg/L
<i>E.coli</i>	Nil/100	Nil/100	Nil/100

APPENDIX 4

Statistical Analysis of Elwak Borehole

Parameters	Elwak	WHO	NEMA
pH	7.67	6.5-8.5	6.5-8.5
Electrical conductivity	6940 $\mu\text{S/cm}$	2000 $\mu\text{S/cm}$	2400 $\mu\text{S/cm}$
Total dissolved solids	4302 mg/L	1000 mg/L	1200 mg/L
Fluoride	1.0 mg/L	1.5 mg/L	1.5 mg/L
Chloride	119.9 mg/L	250 mg/L	No guideline value
Ammonium-NH ₄ ⁺	0.0 mg/L	No guideline value	0.5 mg/L
Nitrate NO ₃ ⁻	1.898 mg/L	50 mg/L	10 mg/L
Sodium	46.4 mg/L	No guideline value	No guideline value
Potassium	101.4 mg/L	No guideline value	No guideline value
Lead	Not detected	0.01 mg/L	0.05 mg/L
Zinc	189 $\mu\text{g/l}$	3mg/L	1.5 mg/L
<i>E.coli</i>	Nil/100	Nil/100	Nil/100

APPENDIX 5

Statistical Analysis of ShimbirFatuma borehole

Parameters	ShimbirFatuma	WHO	NEMA
pH	5.3	6.5-8.5	6.5-8.5
Electrical conductivity	1107 $\mu\text{S}/\text{cm}$	2000 $\mu\text{S}/\text{cm}$	2400 $\mu\text{S}/\text{cm}$
Total dissolved solids	686 mg/L	1000 mg/L	1200 mg/L
Fluoride	0.6 mg/L	1.5 mg/L	1.5 mg/L
Chloride	7.99 mg/L	250 mg/L	No guideline value
Ammonium-NH ₄ ⁺	0.0 mg/L	No guideline value	0.5 mg/L
Nitrate NO ₃ ⁻	2.86 mg/L	50 mg/L	10 mg/L
Sodium	35.4 mg/L	No guideline value	No guideline value
Potassium	12.3 mg/L	No guideline value	No guideline value
Lead	Not detected	0.01 mg/L	0.05 mg/L
Zinc	67 $\mu\text{g}/\text{l}$	3mg/L	1.5 mg/L
<i>E.coli</i>	Nil/100	Nil/100	Nil/100