University of Venda

Determination of anions and cations in natural water

by

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A dissertation submitted in fulfilment of the requirements for the
Master of Science degree
in the
School of mathematical and natural sciences
Department of chemistry
Analytical chemistry project (CHE 6000)
(Student number)
15005219

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Declaration

I, NETSHIFHEFHE HUMBELANI KELLY, hereby, declare that this study is my own work and was not taken from other sources without acknowledgement.

Signature………………………….. Date ……………………

Acknowledgements

Firstly, I would like to thank God, for enabling me and for giving me strength and courage to start and finish this thesis. I would like to acknowledge,

1. My Supervisors, Prof IDI Ramaite and Mr LR Puka for all their academic guidance and support.
2. Furthermore, I would like to express my appreciation to my family and friends, especially my parents Mr ND Netshifhefhe and Mrs L Netshifhefhe who supported me and encouraged me throughout the period of study.
3. I would like to acknowledge Dr NT Tavengwa for his mentorship and assistance, Mr K Chigayo, Mr AT Gordon, Dr M Nomvano, Mr FB Mutshaeni, Mr S Ncube, Mr M Dube Johnstone and Mr S Karambwe for all the assistance and guidance with lab work and write-up.
4. I would also like thank the Sasol Inzalo-National Research funding (NRF) and university of Venda research and publication committee (RPC) for their financial support.

Abstract

Surface water is used for domestic and agricultural activities in Musina region and other surrounding areas. This is because of the shortage of potable water. As a result, the people living in the region and its surrounding areas are potentially exposed to hazardous contaminants that may be present in the surface water. It is therefore important to ascertain the quality of the surface water in the region.

Surface water samples were collected from Mutale, Nwanedi, Tshipise and Nzhelele rivers. The samples were analysed for anions such as fluoride (F^-), chloride (Cl^-), nitrate (NO_3^-), phosphate (PO_4^{3-}), sulphate (SO_4^{2-}); cations such as aluminium (Al), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), sodium (Na) and trace metals such as lithium (Li), vanadium (V), chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), molybdenum (Mo), cadmium (Cd), thallium (Tl) and lead (Pb) by using analytical techniques such as IC, ICP-OES and ICP-MS. The same samples were also investigated for other parameters such as pH, temperature, EC, TH, TDS, Na % and SAR. The WHO (2008), SANS 241 (2006) and Canadian guideline (2017) were used as a water quality guideline for drinking purposes.

Higher concentrations of Li, V, Cr, Ni, Cu, Zn, Al, Ca, Mg, K and Na in river water were detected in rainy season, whereas higher concentrations of As, Mo, K and Fe were recorded in dry season. The concentration of F^-, Cd, Tl and Pb showed low contamination level in river samples. The results demonstrated that Tshipise river water was contaminated with high concentration of parameters: TDS (1864.0.8-3372.8 mg L^{-1}), EC (2960.3-5270 mS cm^{-1}), F^- (6.403-8.419 mg L^{-1}), SO_4^{2-} (289.657-326.598 mg L^{-1}), Na (836.690-922.810 mg L^{-1}) and As (10.017-11.267 µg L^{-1}) and relative to the (WHO) water guidelines. Nwanedi river also showed higher values of EC (298.0-699.0) mS cm^{-1} and TDS (190.3-447.5) mg L^{-1}. In this study, the results indicated that water from Tshipise and Nwanedi river is not suitable for human consumption based on the guidelines of drinking water. The results also indicated that the soil sample had abundance of Ca, Al, Mn and Fe with concentration ranging from 0.13-10595, 0.0084-4.16, 0.0455-1116.5, 2.4-287404 mg Kg^{-1} respectively.

Keywords: anions, cations, trace metals, IC, ICP-MS, ICP-OES, WHO and surface water.

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Abbreviations

AAS	Atomic absorption spectroscopy
EC	Electro-conductivity
EPA	Environmental Protection Agency
GC-MS	Gas chromatography mass spectroscopy
GFAAS	Graphite flame atomic absorption spectroscopy
IC	Ion chromatography
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
ICP-MS	Inductively coupled plasma- mass spectroscopy
ICP-OES	Inductively coupled plasma-optical emission spectrometer
ISE	Ion selective electrode
MAL	Maximum allowable limit
MCL	Maximum contaminant level
meq L^{-1}	Milli equivalents per Litre
mg L^{-1}	Milligrams per litre
mS m^{-1}	Millisiemens per meter
Na %	Sodium percent
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
POPs	Persistent organic pollutant
SABS	South African bureau of standards
SANS	South African national standards
SAR	Sodium adsorption ratio
TDS	Total dissolved Solids
TH	Total hardness
USEPA	United states environmental protection agency
WHO	World health organisation

Chapter 1: Introduction

This chapter introduces the study and describes the occurrence of anions and cations of water around the world, aims and objectives of the study.

1.1 Background

Natural water is one of the most consumed resource around the world, which plays an important role in everyday life of all living species. It is also an important source of essential elements such as iron, zinc, copper and calcium among others. Edokpayi et al. (2015) indicated that about 1.1 billion people in the world lack basic access to clean, safe and adequate water resources and 85% of them live in rural areas. The inadequacy of water supply has resulted in water-related diseases that triggered most illnesses around the world (Landrigan et al., 2017). According to Kahinda et al. (2007), South Africa has 9.7 million of the people who do not have access to adequate water supply and about 3.7 million people have no access to any form of water supply infrastructure. However, according to Edokpayi et al. (2016) surface water has been used as a main source of water for different purposes, which include drinking, irrigation, animal farming, recreation and serves as habitat to numerous organisms.

Over the past years, South Africa has been experiencing water shortage and no proper supply of clean water in rural areas. This has led to the increased use of water from the rivers, dams and boreholes for domestic purposes, irrigation and other agricultural activities (Calisevici et al., 2009). However, this water is often contaminated with toxic substances (Kolpin et al., 2002; Shen et al., 2001). Exposure to trace and toxic elements often occur through drinking water. Water contains inorganic anions such as fluoride, chloride, nitrate, phosphate and sulphate and cations such as aluminium, calcium, iron, potassium, magnesium, sodium, lithium, vanadium, chromium, cobalt, nickel, copper, zinc, arsenic, molybdenum, cadmium, thallium, and lead that can be toxic to all living organism depending on their levels of concentration.

Several international and local researchers have investigated these elements in groundwater and surface water in South Africa and other parts of the world (Brima, 2017; Wright et al., 2014; Calisevici et al., 2009; Ncube and Schutte, 2005; Coetzee et al., 2004). Heavy metals are attracting more attention in the environmental, toxicological and pharmaceutical analysis. Metals are comprised of macro and trace elements. According to Ali et al. (2014), water contains macro elements that are necessary to sustain biological life. Trace elements are those elements occurring in low concentrations (< mg L^{-1}). Some of the trace elements are essential for plant and animal growth (He et al., 2005). However, some of the heavy metals are toxic to the environment at high concentrations, hence are considered contaminants (Sami and Druzynski, 2003). Some anions such as chloride and sulphate are considered secondary contaminants since; they do not necessarily have a risk to human health but can affect the tastes, colour, odour and appearance of drinking water (Blas II, 2015; Jackson, 2000).

Water containing high concentration of cations and anions that are above the set guideline standards can be dangerous for aquatic species and toxic to the environment. The South African bureau service (SABS) and world health organisation (WHO) specified the maximum contaminant level (MCL) for a number of inorganic anions and cations. The MCL helps to regulate the health effect arising from the ingestion of these anions and cations in drinking water (Jackson, 2000). The maximum amount of contaminants of the ions are set by the drinking water quality regulatory standards in relatively low ng L^{-1} to mg L^{-1} ranges.

Moreover, consumption of contaminated water results in health problems, diseases and sometimes death. A recent study done by Landrigan et al. (2017) has indicated that water pollution (soil, water and air) kills three times more than diseases such as TB, HIV and malaria combined. According to Ayoob and Gupta (2006), around 200 million people from 25 nations are under a dreadful fate of fluorosis. India and China are two most populous countries of the world, which are affected (Ayoob and Gupta, 2006).

There are various reasons as to why researchers have assessed the water quality. Some of the reasons include water as one of the most important resources used by humankind on daily basis. Water pollution by heavy metals and organic pollutants has become common. Increasing use of pesticides, herbicides and manure containing anions and heavy metals in agricultural soil results in potential harm to mankind and the environment in general (Lui, 2011). The sources of contaminants in water are from human activities such as sewage effluents, pharmaceuticals, dyestuffs, perfumes, detergents, industries, dumbed mines and agricultural runoffs. Therefore, this study is aimed at investigating the concentration of major and trace elements in surface water of the upper region of Limpopo (Mutale, Nwanedi, Tshipise and Nzhelele), South Africa.

1.2 Distribution of anions and cations in water around the world

1.2.1 International

Akan et al. (2014) studied levels of fluoride, cadmium, arsenic, lead and nickel in sachet, tap and groundwater of Maiduguru Metropolis of Borno state in Nigeria. The study has shown that high concentrations of fluoride (1.65 mg L^{-1}) were detected in people within the age 51-60. However, low concentrations of 0.002 mg L^{-1} were determined in female subjects within the age group 1-10 years.

Agbalagba et al. (2011) studied physico-chemical properties and hydrochemical processes of groundwater. Samples were collected from eight commercial boreholes in Yenangoa, Bayelsa state in Nigeria. The samples were analysed for the physico-chemical parameters such as pH, EC, BOD and elements such as Ca, Fe, Cu, Cr, Cd and As of which Fe exceeded WHO drinking water permissible limit. All other metals were below detection limit except for Fe.

Akan et al. (2010) investigated the physical and chemical parameters in Abattoirs wastewater sample in Malduri Metropollis, Nigeria. Samples were collected for the determination of pH, temperature, turbidity, conductivity, total suspended solids (TSS), TDS, dissolved oxygen, chemical oxygen demand (COD), biochemical oxygen demand (BOD) and anions such as chloride, nitrate, sulphate, phosphate. Heavy metals such as Cd (0.74 µg L^{-1}), Pb (0.36 µg L^{-1}) and Ni (0.41 µg L^{-1}) were exceeding WHO and the United States Environmental Protection Agency (USEPA) standard of drinking water concentration (0.30, 0.10 and 0.10 µg L^{-1} respectively). The values of turbidity, nitrate, TSS and TDS were also found to be higher than the WHO permissible limits.

Hasan and Ali (2010) determined the occurrence of manganese in Bangladesh groundwater. High manganese concentrations in groundwater have been found in the central, northern, and western regions of Bangladesh. Groundwater in the Northeastern region of Bangladesh contain relatively less manganese. Deeper wells (> 150 m) have been found to contain relatively lower concentrations of Mn. Areas with low arsenic in groundwater have been found to contain high manganese concentrations and vice versa.

Bishnoi and Malik (2008) studied the systematic physico-chemical properties of the groundwater at 41 different locations in Panipat city (Haryana), India to evaluate its suitability for domestic purposes. Their study revealed considerable variations in the water samples with respect to chemical composition and they found that all samples have high concentration of dissolved salts.

Kar et al. (2008) studied the assessment of heavy pollution in surface water in West Bengal. Surface water samples (96) were collected from Ganga river. Samples were collected for the assessment of pH, EC and metals such as Fe, Mn, Zn, Cu, Cd, Cr, Pb and Ni. A significant negative correlation was observed between Fe and Cr, whereas Ni exhibited a significant positive correlation with Mn and Zn.

Goel (2006) investigated concentration of lead and arsenic in sediments and well water from Domodar, Safi, Ganga, Adjai rivers of Jharkhand and west of Bengal. However, high levels of contamination by heavy metals, chemicals, organic matter, nitrates, human and animal excreta were found in various rivers in India including Ganga, Yamuna, Gomiti, Ramganga, Hindon, Chambal, Godavari, Krishna, Sabarmati, Subernrekha and Cauvery.

1.2.2 National

Mpenyana-Monyatsi and Momba (2012) assessed the quality of the groundwater in rural communities of the North West Province. All boreholes samples from the rural areas were analysed for physico-chemical parameters such as pH, temperature, TDS and concentrations of chloride, sulphates, nitrate, fluoride, magnesium, sodium and calcium. The results revealed that 83% of the boreholes did not comply with the fluoride limit of SANS 241, 40% did not comply with the nitrate limit, 45% did not comply with the magnesium limit, 43% did not comply with the calcium limit, 31% did not comply with TDS and 47% did not comply with the turbidity limit.

Ncube and Schutte (2005) specified that a survey conducted by the Department of Water Affairs and Forestry (DWAF) indicated that there are many boreholes in the country that contains the concentration of fluoride, nitrate, sulphates and heavy metal that pose a health risk if this water is used for drinking purposes. Ncube and Schutte (2005) identified Limpopo, Northern Cape, North-West and KwaZulu-Natal Provinces as areas with high contamination of groundwater in South Africa.

Fatoki and Awofolu (2003) conducted a study in Umthatha river and dam. The study was carried out for the determination of trace metals such as Cd, Hg and Zn in surface water and sediments. Buffalo, Keiskamma and Tyume rivers contained elevated levels of Cd, with normal concentration of Hg and Zn in samples of surface waters.

1.2.3 Local

Edokpayi et al. (2017) studied temporary seasonal variation of heavy metals and their potential ecological risk in Nzhelele River, Limpopo Province. The concentration of heavy metals (Al, Cd, Cr, Fe, Mn, Pb, Cu and Zn) were assessed by using ICP-OES. Higher concentrations of Fe, Mn, Pb, Cu and Zn were determined in the dry season in the river water.

Edokpayi et al. (2016) also assessed the variation pattern in trace metals contamination in Mvudi River water for the period of January-June 2014. Metal concentrations were analysed using an ICP-MS. The pH and EC ranged from 7.2-7.7, 10.5-16.1 mS m^{-1} respectively. The monthly average levels of trace metals in the of water of Mvudi river were in the range of: Al (1.01-9.644 mg L^{-1}), Cd (0.0003-0.002 mg L^{-1}), Cr (0.015-0.357 mg L^{-1}), Cu (0.024-0.185 mg L^{-1}), Fe (0.702-2.645 mg L^{-1}), Mn (0.081-0.521 mg L^{-1}), Pb (0.002-0.042 mg L^{-1}) and Zn (0.031-0.261 mg L^{-1}).

Edokpayi et al. (2015) investigated temporal variations in physico-chemical and microbiological characteristics of Mvudi river, Limpopo Province. The study identified the following physiochemical properties: pH, EC and turbidity values were in the range of 7.2-7.7, 10.5-16.1 mS cm^{-1} and 1.3-437.5 NTU respectively. Selected anions fluoride, chloride, nitrate and sulphate were also determined to have the concentration of (0.11 mg L^{-1}, 0.27 mg L^{-1}, 9.35 mg L^{-1}, 14.82 mg L^{-1}, 3.25 mg L^{-1} and 6.87 mg L^{-1}, 3.24 mg L^{-1} and 0.70 mg L^{-1} respectively.

Edokpayi et al. (2016) evaluated the water quality of Dzindi river in Limpopo Province. The river was analysed for following physico-chemical parameters: pH, EC, TDS and the concentrations of the selected heavy metals Al, Cr, Cu, Fe, Mn, Pb, and Zn were determined by using a Perkin Elmer FAAS. The pH, EC and TDS values ranged from 7.47-7.53, 30-133 mS cm^{-1} and 20.10-89.11 mg L^{-1} respectively. The order of heavy metal contamination followed the trend: Fe (1.33 mg L^{-1}) > Al (0.3 mg L^{-1}) > Mn (0.15 mg L^{-1}) > Zn (0.10 mg L^{-1}) > Cr (0.06 mg L^{-1}) > Cu (0.05 mg L^{-1}) > Pb (0.03 mg L^{-1}). Results from this investigation reveals that Dzindi river was contaminated with heavy metals.

Mhlongo and Amponsah-Dacosta (2014) studied the assessment of safety status of open excavations and water quality of pit lake at abandoned Nyala Mine in Limpopo Province of South Africa. The water in the pit was found to be alkaline (pH ±9.6) with F^- (±1.1 mg L^{-1}), Cl^- (±169.6 mg L^{-1}), Mg^{2+} (±67.85 mg L^{-1}) and K^+ (±87.16 mg L^{-1}) concentrations that were all above the standards permissible for domestic use.

Samie et al. (2013a) studied the physical and chemical quality of several borehole water in rural schools of Greater Giyani Municipality. Samples were collected to assess pH and ions such as magnesium, calcium and chlorides. Atomic absorption spectroscopy and ion chromatography were used to determine the chemical quality of water. pH varied between 5.29 and 8.3, fluorides and phosphate were not detected from all schools. In addition, chloride and sulphate were within DWARF limits.

Odiyo and Makungo (2012) studied the concentration of anions and cations in water of the Nyala mine, Limpopo. Samples were collected for the determination of F^-, Cl^-, K^+ and Mg^{2+}. The following were the concentration of metal: 1.1 mg L^{-1}, 169.6 mg L^{-1}, ± 87.16 mg L^{-1} and ± 67.8 mg L^{-1} respectively. Water of the Nyala mine in Limpopo Province has recently been found to be above the standard DWAF permissible limits for domestic use.

Onyango et al. (2010) investigated natural zeolite and its potential for treating drinking water containing excess amount of nitrate. Samples were collected in Lesedi Motlala, Tshiozwi and Sekhokho. The study indicated that elevated nitrate concentration in drinking water lead to the production of nitrosamines.

Okonkwo and Mothiba (2005) studied trace metal analysis of the surface waters from Dzindi, Manedzhe and Mvudi river, South Africa. The study was conducted by using Varian FAAS for the analysis of Cd, Cu, Pb and Zn. The concentration of Cd, Cu, Pb and Zn ranged from 1.6-9.3, 2.0-3.0, 10.5-20.1 and 2.1-2.5 μg L^{-1} respectively.

1.3 Motivation of the study

The quality of water resources is a subject of ongoing concern and yet the assessment of long-term water quality changes is a challenging problem. Water sustains life and is an important source of essential elements. Exposure to trace and toxic elements often occurs through drinking water (Kavcar et al., 2009; Martin and Griswold, 2009; Järup, 2003; Jain and Ali, 2000; Tchounwou, 1999). According to Schwarzenbach et. al. (2006) about one-fifth of the World's population does not have access to safe water and about 15% of the World's population lives in areas of water stress. In developing countries, most rural communities depend on surface water such as wells, ponds, springs and rivers for domestic and agricultural purposes (Edokpayi et al., 2015; Odumo et al., 2011; Oberholster and Ashton, 2008a). Surface water has been a source of domestic water due to shortage of potable water in most rural areas, although water from rural areas often receives partial or minimal treatment. Surface water may accumulate heavy metals that are beyond the drinking water permissible limit and which then causes risks to human health, plants, animals, and the environment. The accumulation of metals and ions in the aquatic environment has direct consequences on the water system.

Increasing contamination caused by industry, urbanization, mining and agriculture are playing a big role in polluting the water bodies (Bogardi et al., 2012; Singare et al., 2012). Agricultural practices (runoff from the application of pesticide, fertilizers and herbicides) are the major source of heavy metals in water. However, other elements such as fluoride, sulphate and chloride occur naturally in rocks. Effluent and release of some waste from the community, mines and industries close to the water bodies cause harm in the aquatic system and affect the food chain. Contaminated water may cause diseases such as fluorosis and cancer (Edokpayi et al., 2015; Gamage et al., 2010; Suleiman et al., 2009; Odiyo et al., 2005; Ncube and Schutte, 2004; Phillips and Bode, 2004; Fatoki and Awofolu, 2003). Inorganic contaminants and heavy metals are getting attention for their non-degradable and toxic nature in the aquatic environment. There are risks to health problems brought by long time consumption of surface water. High toxicity has created a pressing need for effective monitoring and measurement of pollutants in water.

Concern about environmental and health issues related to water makes it important to understand the possible hazards associated with their use and to minimize the risk. There are several studies done on drinking water quality in South Africa (Edokpayi et al., 2015; Ali, 2010; Kahinda et al., 2007; Coetzee et al., 2004; Fatoki and Awofolu, 2003). However, there are few reported studies on rivers such as Mutale, Nwanedi, Tshipise and Nzhelele river found in the upper Vhembe region. Mutale, Nwanedi, Tshipise and Nzhelele are the areas found in the Northern part of Limpopo in the Vhembe district. These villages still practise subsistence farming and still depend on natural water for drinking, fishing and domestic activities. However, most rivers are located near farming and mining areas**.** There are no portable water supplies in some of these areas. Hence, dependence on water sources mainly from ground and surface waters for domestic, irrigation and livestock activities. Therefore, regular monitoring of the drinking water quality is necessary. This study will focus on determining the physico-chemical parameters and concentration of different ions and metals in rivers of the upper Vhembe regions.

1.4 Aim and objectives

1.4.1 Aim

The aim of this project is to determine selected anions and cations in natural water around Musina region.

1.4.2 Objectives

- To collect water samples from potentially contaminated areas
- To investigate physico-chemical parameters in the water sample
- To evaluate the concentration of specific anions and cations present in the water by using analytical techniques such as IC, ICP-OES and ICP-MS
- To compare the concentration of anions and cations in different seasons with that of the WHO standard values.

Chapter 2: Literature review

This chapter includes the description of sources of chemical constituents in water, factors affecting water quality, occurrence and health effects of anions and cations that are of concern. It also presents the water quality standards guidelines such as WHO, SANS and Canadian drinking water guideline. This chapter also gives the description of the techniques and sampling method.

2.1 background

The presence of toxic metals and anions in the environment is becoming very problematic and worrying, because of the health implications of the anions and cations have on humans (Musa et al., 2008). As Schwarzenbach et al. (2006) indicated that increasing contamination of freshwater systems with industrial and natural chemical compounds are some of the sources of the ongoing environmental problem the society is still facing. The chemical constituents of surface water have an influence on crop production and health of those depending on water (Schwarzenbach et al., 2006; Awofolu et al., 2005; Carpenter et al., 1998). Although some of these constituents are present at low concentrations, many of them raise extensive toxicological concern.

2.2 Sources of chemical constituents in water

2.2.1 Naturally occurring sources

Heavy metals contamination to the terrestrial environment has long existed due to the natural weathering of the parent rocks which causes metal precipitation in the system (Lui, 2011). Naturally occurring rocks are divided into three types depending on how they are formed, for example, igneous rocks, sedimentary rocks and metamorphic rocks (Mibei, 2014). Igneous rocks are formed by the solidification and cooling of magma in volcanic areas, while
sedimentary rocks are formed by low temperature accumulation of sediments in tectonic basins and topographical sinks. Metamorphic rocks, on the other hand, are formed by application of temperature and pressure on pre-existing rocks (Mibei, 2014). However, rocks such as metamorphic rocks are highly exposed to the surface environment through the process of weathering and erosion. Temperature plays a role in the weathering of rocks. These rocks, however, contains minerals such as (diorite, quartz, amphibole, etc) and salts that may be toxic to the environment if available in excess. These minerals contain anions and elements such as

Cl^-, SO_4^{2-}, Na, Ca, K, Fe, Mg and metal such a Zn, As, Cd, Tl and many more. Some of the metals are naturally occurring in the soil environment by processes of weathering of parent materials at levels that are regarded as trace and rarely toxic (Wuana and Okieimen, 2011; Fatoki and Awofolu, 2003). The problem comes when these rocks containing minerals through weathering process breaks down and leach into surface water, where they are dissolved. Figure 2.1 below shows a brief summary of how ions and metals reach surface and groundwater, of which naturally occurring rocks and soil containing minerals as well as anthropogenic sources are part of the water contamination circle. Rivers also contribute to the main water resources in areas for drinking, irrigation and industrial purposes.

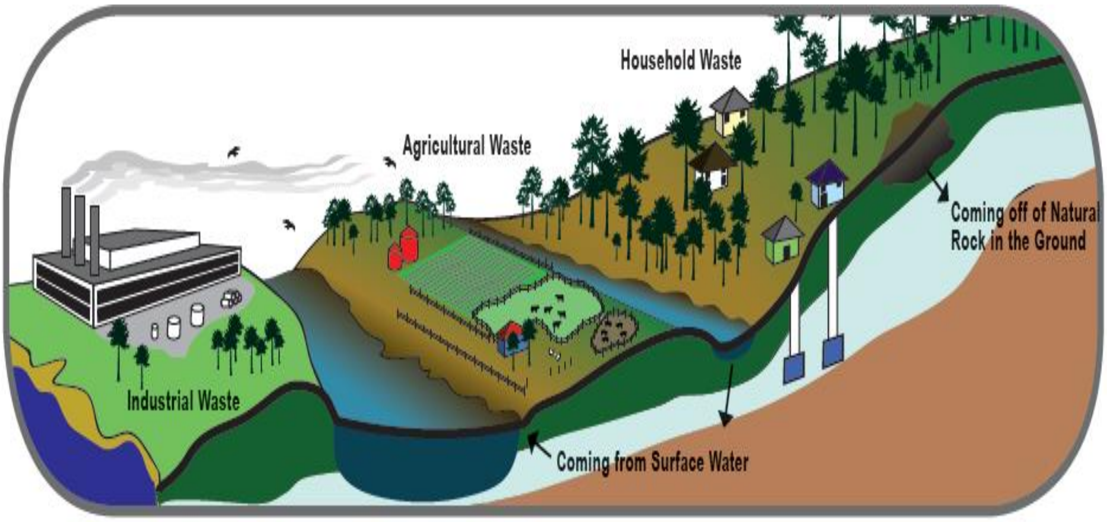

Figure 2.1: Water contamination circle (NC department of health and human services, 2011)

2.2.2 Anthropogenic and Agricultural sources

Water may become contaminated by the accumulation of ions and heavy metals from emissions of industrial waste, domestic waste, wastewater treatment plants, agricultural practices (application of fertilizers, pesticides, manures and insecticides), coal combustion residues, spillage of petrochemicals, and atmospheric deposition (Al Nouri et al., 2014; Wuana and Okieimen, 2011). Farmers use fertilizers and pesticides on daily basis to increase soil fertility and crop production. However, most fertilizers happen to contain ions and heavy metals such as (As, Cd, Cr, Cu, Pb, Ni, Mo, Zn, Tl and Fe) that can be toxic on the environment (Laar et al., 2011). Fertilizers containing heavy metals in the soil are adsorbed by initial fast and slow adsorption reactions, then redistributed into different chemical forms with varying bioavailability, mobility, and toxicity (McDowell et al., 2001). Water is an excellent solvent and transport medium for particulates and therefore becomes contaminated by natural dissolution of salts that are geologically present in soils (Hohls et al., 2002). Anthropogenic trace-elements deposited on soils from fertilizers and pesticide also cause persistent problems in the industries (Gleyzes et al., 2002). The increasing chemical pollution of surface water, with long term effects on aquatic life and human, could easily lead to a problem of greater magnitude (Schwarzenbach et al., 2010; Schwarzenbach et al., 2006). Chemical pollution of natural waters has already become a major public concern nationally and internationally. Some elements are essential and important for our daily dietary (de Almeida Pereira et al., 2004), however constant consumption of high concentration may have adverse health effects. Heavy metals above drinking water quality guidelines may cause risks to human health, plants, animals, ecosystems (Duruibe et al., 2007; Awofolu et al., 2005).

Plants must acquire not only macronutrients (N, P, K, Ca, and Mg), but also essential micronutrients. Some soils contain low concentration of heavy metals (such as Co, Cu, Fe, Mn, Mo, Ni, and Zn). Excessive application of fertilisers, manures and persistent organic pollutants (POPs) are really affecting the water environment. POPs are organic compounds that are resistant to environmental degradation through chemical, biological and photolytic processes and have long half-lives in soils and sediments (Jones and De Voogt, 1999). Many POPs are used in industrial production. Some of these chemicals proved beneficial in pest and disease control, crop production and industry (Schwarzenbach et al., 2006; Awofolu et al., 2005; Carpenter et al., 1998). Some of the Examples of POPs are chlorinated (organochlorine pesticides), brominated aromatics, polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). Pesticides are used for crop and weeds protection in farming. Pesticides can also be applied to crops to increase their yield (Al-Rimawi, 2014). Pollution by agricultural chemicals has become a growing concern worldwide (Asi et al., 2008). Some of the pesticides are to bind more to the soil but these on the other hand through soil degradation, weathering and rainfall may pollute surface water.

2.2.3 Industries and mining

Effluents and emission from industries and mining sectors are released into wastewater, air and the environment. Combinations of industrial contaminants with rain find their ways into soil, surface and groundwater. The most abundance heavy metals found in soil are Pb, Cr, As, Zn, Cd, Cu, and Hg (Adelekan and Abegunde, 2011; Wuana and Okieimen, 2011). These metals could be harmful to the environment if available in excess, although, they can be applied in the soil to promote growth, protection and high productivity of crops. According to Wuana (2011), most metals such as Pb, Cr, As, Zn, Cd, Cu, Ni occurs in the environment as a byproduct from mines and industries (Wuana and Okieimen, 2011; He et al., 2005). Kabala et al. (2009) investigated the concentration of metals (Pb, Zn and Cu) close to industry. Heavy metals are considered serious pollutants because of their toxicity, persistence and non-degradable conditions in the environment (Nwuche and Ugoji, 2008; Tam and Wong, 2000). Ions from the soil, industrial, agricultural and household waste are transported into streams and waterways (G. Georgopoulos, 2001). Dumbed mines, acid mine water drainage, leakage or flow of mineral exposed surface water are a serious concern to the environment sources resulting in an increment of chemical constituents in the water (Hota, 2014). Mines have the potential to release harmful substances into the soil, air and water. As water takes on harmful concentrations of minerals and heavy metals, it becomes contaminated.

2.3 Factors that affect the quality of water

The quality of water describes the physical, chemical and aesthetic properties of water to regulate the suitability for use. Chemical constituents such as ions and heavy metals that are dissolved or suspended in water influence many of these properties. Anions and cations are affected by the environmental conditions such as pH, temperature, electro-conductivity, total dissolved solids and climatic conditions (Ali et al., 2014).

2.3.1 pH

pH value in water measures acidity and alkalinity of water. Water with a pH value of <7 is acidic and with pH value >7 is basic. The pH of the water bodies determines the chemical species of many metals thereby altering their availability and toxicity in aquatic environments (Melamed, 2005). pH value below 7 accelerates corrosion rate of metallic substances in water (Pradhan and Pirasteh, 2011). pH is affected by factors such as heavy metals, rocks salts and ions in the water. However, some type of rocks such as limestone can neutralize the acid. The pH of a solution can affect the toxicity of other elements and chemical reactions which are important in industry, irrigation and domestic water treatment (Pradhan and Pirasteh, 2011). Surface water has a pH value of between 6.5 and 8.5 (Oberholster and Ashton, 2008).

According to the (SANS241, 2006) drinking water quality, the pH of drinking water should be between 6.5-8.5. Natural water containing acid can harm or even kill aquatic plants and animals. Acidic water is also not good for the human consumption since it causes health problems such as eye and skin irritation. A decrease in pH rises the solubility of metals, for example, weathering and solubility of minerals (limestone or dolomite) in water becomes more rapid if pH is low. However, high pH values tend to precipitate the heavy metals as hydroxides (Abegaz, 2005). The coexistence of species depends on pH, redox potential and ionic strength of the system. pH is important in maximizing water treatment effectiveness, controlling corrosion and reducing leaching from the distribution system and plumbing components (Canada, 2017). Table 2.1 below shows the effects of pH on water adopted from (Organization, 2004).

Table 2.1: Effects of pH on water

pH	Effect of pH on water
<4	May cause danger to human, because at this pH most toxic metals and ions are dissolved. These also cause the water to be salty Dissolve toxic metals
4-6	Water taste salty
6-9	Metals are unlikely to dissolve at the pH range 6-9 unless there are complexing ions or agents are present.
>9	Difficult to disinfect

2.3.2 Electro-conductivity and total dissolved solids

Electro-conductivity (EC) is a measure of dissolved ions or inorganic materials including calcium, bicarbonate, nitrogen, phosphorus, iron, sulphur, magnesium, sodium, and potassium, hydrogencarbonate, chloride, sulphate and nitrate (Dikole M, 2014; Cheepi, 2012). Water containing 150-300 mS cm^{-1} is considered very salty and may have some effects on plumbing and appliances. High EC coupled with temperature increases the toxicity of metals. Water containing high EC has negative domestic, industrial and agricultural effects (Cheepi, 2012). Amount of mineral and salt impurities in the water are called total dissolved solids (TDS).

Total dissolved solids ranges from 0 to > 2000 mg L^{-1} and can be determined quickly by measuring the electrical conductance of water samples or by evaporation of filtered samples of water and weighing the residue (Cheepi, 2012). Total dissolved solids in drinking water originates from natural sources, sewage, agricultural runoff and industrial wastewater and if high may results in excessive scaling in water pipes, water heaters, boilers and appliances (Canadian guideline, 2017; WHO, 2008). High concentrations of TDS limit the suitability of water as a drinking source and irrigation supply (Abegaz, 2005). Consumption of water containing high TDS value can result in health hazards such as diarrhoea, joint pains, skin allergies, gastrointestinal disturbances, and vomiting (Cheepi, 2012). Other effects TDS has on the environment are shown below in Table 2.2 (WHO, 2004a). According to Pradhan and Pirasteh (2011), TDS can be calculated using the relationship given below:

$$\text{TDS (mg L}^{-1}\text{)} = \text{EC (mS cm}^{-1}\text{)} \times 0.64$$

Table 2.2: Effects of EC on water and the environment

Threshold (mS m^{-1})	Effect of electro-conductivity in water
0-70	No health effects associated with this EC threshold
70-150	Water has a salty taste. No effects on plumbing or appliances. No health effects are likely to occur.
150-300	Water is salty and cannot be used for aesthetic reason. Affect and cause corrosion on plumbing and appliances. No adverse short term effect in living organism.
300-450	Water has extremely salty taste and can cause corrosion.
>450	Water tastes extremely bitter and salty. Increase scaling of corrosion. Short term consumption leads to disturbance of body salt balance. At high concentration, short term health effects are expected.

2.3.3 Climatic conditions and temperature

Some arid and semi-arid areas experience erratic and unpredictable extremes of drought and floods (Oberholster and Ashton, 2008). This, however, affects the water system if these water bodies experience high rates of evaporation and precipitation of salts in the water. The inflows and outflow in the river and amount of the water in the river plays an important role in the precipitation, solubility and evaporation of the ions in the water bodies. Evaporation and precipitation are mostly influenced by temperature. These affect the concentration of anions and cations. These conditions result in eutrophication because of high availability of some ions such as phosphate, sulphate and nitrate. High water temperature enhances the growth of microorganisms and may increase taste, odour, colour and corrosion problems (Organization, 2008). Increasing temperatures tend to elevate the solubility and toxicity of dissolved metals, while dissolved oxygen levels generally decrease with increasing temperature (Abegaz, 2005).

2.4 Uses and occurrence of anions and cations in the environment

2.4.1 Fluoride

Fluoride is an important micro-nutrient that can be available in small concentrations (Rafique et al., 2009), but becomes toxic at high concentrations. Fluoride is a naturally occurring element and can either be obtained from minerals or geo-chemical deposits through the process of natural weathering and leaching (Akan et al., 2014; Bansiwal et al., 2009). Fluorine occurs from minerals such as biotites, fluorspar, cryolite, fluorapatite, amphiboles, topaz and biotite (Edmunds and Smedley, 2013, Organization, 2008). Fluoride in water can be increased by anthropogenic activities such as wastewater from sewage, runoff from agricultural field and naturally occurring rocks and soil erosion (Canada, 2017). Well water may contain up to about 10 mg L^{-1} of fluoride in areas rich in fluoride-containing minerals, although much higher concentrations can also be found (WHO, 2008). Fluoride is mobile under high-temperature conditions (Fetter et al., 2017). Fluoride is used in toothpaste and dentifrices, additive to drinking water and aluminium smelting (Fetter et al., 2017).

2.4.2 Chloride

Chloride is a naturally occurring major anion that is linked with leaching of minerals (gallite, sylvite, carnallite and bischofite) rocks (nephelines) and saline deposits (Dinka et al., 2016). Chloride usually exists in the form of chlorine salts such as NaCl, CaCl and MgCl that are soluble in water. According to WHO, humans becomes exposed to chloride from adding salt to food and drinking water. It is also obtained from dissolved salt deposit, industrial and municipal effluents urban runoff containing de-icing salt and saline intrusion (Dikole M, 2014; Nikanorov and Brazhnikova, 2009; WHO, 2008). Chloride can also be present in air precipitation. High chloride content results in damaging plants, as well as metallic pipes and buildings. The chloride concentration is higher in wastewater than in raw water because sodium chloride is a common article of diet and passes unchanged (Abegaz, 2005). Chloride is used in chemical manufacturing, water purification, shrink-proofing, flame retardants and food processing (Fetter et al., 2017).

2.4.3 Nitrate

Nitrogen occurs in different form of ions such as NH_4^+, NO_2^-, and NO_3^- (Ion, 2014). The ions occurs in water in the form of suspended and colloidal substances and dissolved compounds (Nikanorov and Brazhnikova, 2009). Transformation of organic forms into mineral ores happens in the process of biogenesis whereby element regenerate and result in ammonia being oxidized to nitrites and nitrates (Nikanorov and Brazhnikova, 2009). Nitrates are highly toxic to aquatic life as they easily convert to even more toxic nitrites (NO_2^-). Ammonia ion (NH_4^+) tends to leach slowly but may be converted to soil bacteria to NO_3^- or NO_2^- (Dikole M, 2014). Nitrates are essential in the environment because they are necessary for growth and reproduction of green plants (Abegaz, 2005). Common sources of nitrate pollution are agricultural drainage, manure, feedlot runoff, release of sewage effluents and fertilizers (Canadian, 2017; Abegaz, 2005; Glass and Silverstein, 1998). Some cleaning products contain nitrate that can also form part of water pollution. Abandoning of well fields because of nitrate pollution is continuing and occurring in South Africa (Tredoux et al., 2000). Some groundwater may also have nitrate contamination as a consequence of leaching from natural vegetation (WHO, 2008). It was reported that in most countries, nitrate levels in drinking water obtained from surface water do not exceed 10 mg L^{-1}, although nitrate levels in well water often exceed 50 mg L^{-1} (Ion 2014; WHO 2008). Nitrates are used in fertilizers and food preservatives (Fetter et al., 2017).

2.4.4 Phosphate

Phosphate occurs in the form of suspended colloidal substances, inorganic and organic compounds. Phosphorus, being an anionogenic element, forms phosphoric acid (H_3PO_4) of neutral strength that dissociates into some derivatives forms: $H_2PO_{4,}$ HPO_4^{2-} andPO_4^{3-}. In natural water, phosphorus usually occurs in low concentrations due to low solubility of its compounds and intensive consumption by hydrobiotics (Nikanorov and Brazhnikova, 2009). The sources of phosphate in water include detergents, sewage, industrial wastes, aquifer sediments, agricultural fertilizer, animal waste, and leaking septic systems (Abegaz, 2005; Fuhrer, 1999). Inorganic phosphate in natural waters is primarily present as either orthophosphate or polyphosphate (Abegaz, 2005). Excessive levels of phosphate may lead to the eutrophication (excess growth of algae reduces the oxygen content in the water, which thereof results in plants and fish dying), (Mullins, 2009; Abegaz, 2005). In the oceans, the concentration of phosphates is very low, particularly at the surface (Zhang et al., 2013). Phosphates are used when making detergents, fertilizers and food preservatives (Fetter et al., 2017).

2.4.5 Sulphate

Sulphate mostly exist in a form of sulphates and sulphades in the environment (Cheepi, 2012). The main source of sulphate in water is sedimentary rocks such as gypsum and anhyaride. Sulphate also results from the breakdown of sulphur containing organic compounds (Abegaz, 2005). The process of decomposition and oxidation of substance of vegetables and organic origin containing sulphur plays a role on the increment of sulphur content in the water bodies (Nikanorov and Brazhnikova, 2009). Atmospheric precipitation of sulphate concentration is about 2 mg L^{-1}, however, the concentration in the water bodies varies widely due to oxidation (Cheepi, 2012). Sulphates are used in fertilizers and pesticides (Cheepi, 2012).

2.4.6 Aluminium

Aluminium is one of the most abundant element in the earth’s crust, and constitutes about 8% of the Earth’s crust (WHO, 2008). It is present in drinking water and as dust in the air (Flaten, 2001). Aluminium salts used in water treatment as coagulants to reduce organic matter, colour, turbidity and microorganism levels, which therefore lead to an increment in concentrations of Al (WHO, 2008). Furthermore, during conventional water treatment processes, aluminium undergoes various transformations influenced by factors such as pH, turbidity, temperature of water source, and the organic and inorganic ligands present in water (Srinivasan et al., 1999). Aluminium ion (Al^{3+}) is found in more acidic water. However, aluminium hydroxide ($Al(OH)_3$) shows solubility at pH = 5.07 while aluminate ion (AlO_2^-) is formed at pH= 9.00 values (Galvin, 1996). Aluminium salts are used as a coagulant for purification of drinking water, as a food additive, factories to make alloys, foundry, paints, protective coatings, electrical industry, building and construction machinery and equipment and pharmaceuticals (Fetter et al., 2017, Bondy, 2010).

2.4.7 Calcium

According to Samie et al. (2013b), the most common source of calcium in groundwater is through the erosion of rocks, such as limestone and dolomite, and minerals, such as calcite and magnesite. Water associated with granite or siliceous sand will usually contain less than 10 mg L^{-1} of calcium, from limestone areas may contain 30-100 mg L^{-1}. Those associated with gypsiferous shale may contain several hundred mg L^{-1} (Abegaz, 2005). The average concentration of calcium in streams is about 15 mg L^{-1} (Abegaz, 2005). Calcium is known to reduce the toxicity of many chemical compounds such as (NO_2) on fish and other aquatic life (Dinka et al., 2016). Calcium is always present in every plant, as it is essential for their growth. It is contained in soft tissues, in fluids within the tissue and in the structure of every animal's skeleton. Calcium carbonate solubility is controlled by pH (Abegaz, 2005). Calcium compounds are used in pharmaceuticals, photography, pigments, fertilizers, plasters production of alloys, cements and mortar (Fetter et al., 2017, Abegaz, 2005).

2.4.8 Iron

Iron is one of the most abundant metals in the Earth's crust (WHO, 2008). It is found in combination with other elements called iron ores. The most common iron-containing ores are hematite, magnetite, siderite, limenite and taconite (Ngah and Nwankwoala, 2013; Vasudevan et al., 2009). When combine with oxygen, iron reacts to form rusts. Iron is present in the environment in two oxidation states: reduced soluble divalent ferrous iron (Fe(II)) or oxidized insoluble trivalent ferric iron (Fe(III)) (Ngah and Nwankwoala, 2013). Iron is present in groundwater as ferrous bicarbonate, $Fe(HCO_3)_2$, ferric hydroxide, $Fe(OH)_3$, organic complex iron or corrosion product such as Fe_3O_4 (Ngah and Nwankwoala, 2013). Iron is present in surface waters as salts containing Fe(III) when the pH is above 7. Contamination of water as a result of corroded pipes is common in many cities that have very old water systems (Vasudevan et al., 2009). Iron in water is due to dissolved iron from weathering of rocks and minerals, the landfill leachates, sewage effluents and iron-related and plumbing fixtures (Canada, 2017, Talabi). Iron is used in alloys, machinery, iron and steel industry and magnets (Fetter et al., 2017; Abegaz, 2005).

2.4.9 Potassium

Potassium can also occur in drinking water as a consequence of the use of potassium permanganate as an oxidant in water treatment. Although potassium is nearly as abundant as sodium in igneous rocks, its concentration in groundwater is comparatively very low. This is because the potassium minerals are resistant to decomposition by weathering. The main source of potassium in the environment is be weathering of potash silicate minerals and agro-chemicals (Dinka et al., 2016). Potassium is used in alloys and catalyst (Fetter et al., 2017).

2.4.10 Magnesium

Magnesium is an abundant element in the earth's crust (Abegaz, 2005). The magnesium ion occurs as a result of chemical weathering and dissolution of dolomite, erosion and weathering of rocks (Canadian guideline, 2017; Dinka et al., 2016**.** Magnesium is used in alloys, batteries, electroplating, flash photography, drying agents, fertilizers, pharmaceuticals and foods catalyst (Fetter et al., 2017).

2.4.11 Sodium

Sodium is a naturally occurring element. Sodium also occurs through the process of erosion and weathering of salts deposits and contact with igneous rock (Canada, 2017). Sodium bearing minerals like albite and other members of plagioclase feldspars, nephelene and sodalite are the common source of sodium in the environment (Dinka et al., 2016). Other sources of sodium are effluents and domestic sewage, and agricultural activities (Dinka et al., 2016). Sodium is used in alloys, soap, combination with fatty acids, sodium vapour lamps, to purify molten metals, chemical manufacturing, catalyst, coolant, laboratory reagent and to make glass (Fetter et al., 2017).

2.4.12 Lithium

Metallic lithium will react with nitrogen, oxygen, and water vapour in air. Consequently, the lithium surface becomes coated with a mixture of lithium hydroxide (LiOH), lithium carbonate (Li_2CO_3) and lithium nitride (Li_3N). Lithium hydroxide represents a potentially significant hazard because it is extremely corrosive. The uses of Lithium includes alloys, pharmaceuticals, coolant, batteries and propellants (Fetter et al., 2017).

2.4.13 Vanadium

Vanadium can exist in many oxidation states from +1 to +5 but is mostly found in the +4 and +5. Vanadium is stable in acidic solution below the pH of 2, but is oxidised to the pentavalent state by atmospheric oxygen at higher pH (Pyrzyńska). According to Mampuru et al. (2015), vanadium (V) is more toxic than vanadium (IV). Vanadium in air is released in large quantities from the combustion of fuel and residual oil. Many industrial processes such as steel industries, chemical industries, coal production, and petrochemical industry and phosphate industry causes pollution of vanadium in the environment. Vanadium is used in alloys, catalyst, steel, pigments target material for X-rays (Fetter et al., 2017, Abegaz, 2005).

2.4.14 Chromium

Chromium have a positive influence on the functioning of living organisms, for example Cr(III) is responsible for the appropriate glucose metabolism in animals. Chromium at all pH values is highly soluble in water. Chromium(II) and chromium(III) are less soluble than chromium(IV). Chromium in the environment exists primarily in two oxidation states: Cr(III) and Cr(VI). Chromium(III) is only toxic at high concentrations. Chromium(VI) is a strong oxidizer and is considered toxic to humans and the environment at μg L^{-1} concentrations. Cr(III) exist primarily as a cation in solution and Cr(VI) exist primarily as an anion. These states are reliant on the pH of the solution. If the pH is neutral Cr(III) will form hydroxo-Cr(III) species, whereas at alkaline pH, the hydroxide will precipitate. However, if the pH increases, Cr(III) oxidizes to form Cr(VI), but if the pH level is lowered then it leads to loss of Cr(VI) (Phesatcha et al., 2012). In surface waters, the ratio of chromium (III) to chromium (VI) varies widely. In general, chromium (VI) salts are more soluble than those of chromium (III), making chromium (VI) relatively mobile. Chromium enter in water, air and soil through natural processes and human activities (coal combustion and industrial processes), (Gherasim and Bourceanu, 2013). They easily undergo complexation with various substances present in environmental samples, which are extremely toxic. Chromium is used in metallurgy-alloy, refractory bricks, electroplating, tanning, paint, and wood preservatives (Abegaz, 2005).

2.4.15 Cobalt

Cobalt is a naturally occurring element with one stable isotope ^{59}Co and ^{26}Co known radioactive isotopes. The cobalt exist in three valence states 0, +2, and +3. Because cobalt may occur as a radioactive isotope, it can produce ionizing radiation. Cobalt can be found in a variety of media, including air, surface water coming from leachate of waste sites, groundwater, soil, and sediments, the burning of fossil fuels, sewage sludge, phosphate fertilizers, mining and smelting of cobalt ores, processing of cobalt alloys and industries. Factors affecting the speciation of cobalt in water and sediments include pH and redox potential. Cobalt is used in alloys mainly, pigments, enamels, glazes, electroplating alloys, ceramics, drugs, paints, glass, printing and catalyst (Fetter et al., 2017, Abegaz, 2005).

2.4.16 Nickel

Nickel usually exist in +1, +3 and +4 oxidation states. In the environment, nickel occurs predominantly as the ion $Ni(H_2O)_6^{2+}$ in natural waters at low pH (Wuana and Okieimen, 2011). In neutral to slightly alkaline solutions, it precipitates as to form a stable compound nickelous hydroxide, $Ni(OH)_2$. This precipitate readily dissolves in acid solutions forming Ni(III) (Wuana and Okieimen, 2011). Sources of nickel in rivers are organic matter, minerals, metal plating industries, combustion of fossil fuels, and nickel mining (Singare et al., 2012). The concentration of nickel in drinking water is normally less than 0.02 mg L^{-1}, although nickel released from taps and fittings may contribute up to 1 mg L^{-1} (Canadian guideline, 2017). Nickel is used in alloys, ceramics, batteries, electroplating, catalyst (Fetter et al., 2017).

2.4.17 Copper

Copper is emitted into the atmosphere from both natural and anthropogenic sources. Anthropogenic emission sources include nonferrous metal production, wood production, iron and steel production, waste, industrial applications, coal combustion, non-ferrous metal mining, oil and gasoline combustion, and phosphate fertilizer manufacture (G. Georgopoulos, 2001). Concentrations of copper in drinking water range from <0.005 to > 30 mg L^{-1}, primarily as a result of the corrosion of interior copper plumbing. At levels above 2.5 mg L^{-1} copper imparts an undesirable bitter taste in water; at higher levels, the colour of the water is also impacted (Organization, 2008). Copper is used in electrical industry, alloys, brass, chemical catalysts, anti-fouling paint, algicides and wood preservative.

2.4.18 Arsenic

Arsenic is found widely in the earth’s crust in oxidation states of -3, 0, +3 and +5, often as sulfides or metal arsenides or arsenates (WHO, 2008). In water, it is mostly present as arsenate

(+5). Arsenic comes from many sources in the environment ranging from atmosphere, soil, rocks or natural waters and organisms (Lui, 2011). It originates from natural sources such as geological formations, geothermal and volcanic activity, released from mining, industrial effluent and human activities (Canadian guideline, 2017). Arsenic can exist in the environment as arsenite (As^{5+}) and arsenate (As^{3+}) and both oxidation states are toxic (WHO, 2008). The environmental toxicity effects are consequences of arsenic mobilization under natural processes such as weathering reactions, biological activity and anthropogenic activity (Lui, 2011). Anthropogenic arsenic contamination results from variety of activities; manufacturing metals and alloys, industry practices such as copper or lead smelting, mining, coal burning, refining petroleum and waste (Melamed, 2005; Martin and Griswold, 2009). Arsenic is used in alloys, dyestuffs, medicine, electronic device, insecticides and preservatives (Fetter et al., 2017).

2.4.19 Cadmium

Cadmium is released into the environment through rocks, coal, wastewater and fertilizers (Martin and Griswold, 2009). When taken up by plants, cadmium concentrates along the food chain and ultimately accumulates in the body of people (Singare et al., 2012). Cadmium metal is used in the steel industry and in plastics, batteries, electroplating, pigments, metal coating, thermoplastic stabilizers, PVC, batteries and low melting point alloys (Organization, 2008; Abegaz, 2005).

2.4.20 Thallium

Thallium occurs in two oxidation states, that is, +1 and +3. Tl(III) cations are more reactive and more toxic than Tl(I). Tl(III) ions exist in the solution only when the pH is close to 0. When pH is higher, it causes precipitation. Thallium is introduced into the environment by combustion of coal and as a waste product of zinc, lead and cadmium. The main source of thallium pollution at present is cement production. Thallium application in various types of metal alloys has been increasing. Thallium can be used for various reasons such as catalyst in laser devices, and in the production of optical fibres and high refractive index glass (Voegelin et al., 2015). Thallium is used in alloys glass, pesticides, and photoelectric application.

2.4.21 Lead

Lead often occurs naturally in groundwater due to the weathering of rocks, especially mica and clay. An anthropogenic source is from industries involved in the casing of wells, pipes, and pumps. Lead is released into the soil, groundwater and surface waters in a form of Pb(II), lead oxides and hydroxides, and lead metal oxyanion complexes (Wuana and Okieimen, 2011). The amount of lead dissolved from the plumbing system depends on several factors, including, pH, temperature, water hardness and standing time of the water (WHO, 2008). Lead occurs in the environment from leaching of plumbing pipes, mining and fossil fuel (Canada, 2017; Martin and Griswold, 2009). It is used to produce batteries, ammunition, metal products like solder and pipes, and X-ray shielding devices (Martin and Griswold, 2009).

2.5 Bioaccumulation of anions and cations in the environment

Bioaccumulation is the accumulation of the substance, such as chemical constituents in living organism. It occurs when an organism absorbs a substance at a rate faster than that at which the substance is lost by catabolism and excretion (Alexander, 1999). All these potential hazardous ions accumulate in the environment (air, water, crops and soil) and human bodies, which then creates a serious health concern. Potential health concerns arise from exposure to the toxic substance (anions and cations) through ingestion of drinking water, domestic practices such as (bathing, fishing, washing, and swimming) and through consumption of food and inhalation aswell. The longer the biological half-life of a toxic substance, the greater the risk of chronic poisoning, even if environmental levels of the toxin are not very high (Alexander, 1999). The toxicity of ions depends on several factors including the bioaccumulation, route of exposure, chemical species, dose, as well as the age, nutritional status of exposed organisms (Tchounwou et al., 2012). Residing close to industrial site that manufactures metals and utilises them increases ones risk of exposure (Martin and Griswold, 2009). Metals are highly adsorbed and bioaccumulate in soil, plant (roots, mushrooms and fruits) and in animals (liver, kidney, bones, meat, teeth, skin, nerve tissues and neurons).

2.6 Health effects of anions and cations

2.6.1 Health effects of anions

Drinking water containing high concentration of fluoride higher than 1 or 1.5 mg L^{-1} can cause fluorosis (WHO, 2009; Rafique et al., 2009; SANS 241, 2006; Harrison, 2005; Bo et al., 2003; Li et al., 2003). Fluorosis is a chronic disease that causes teeth to mottle (dental fluorosis) and changes of bone structure (skeletal fluorosis), skin irritation and neurological damage (Akan et al., 2014, Coetzee et al., 2004). However, fluoride is also recommended as a daily dietary, because it reduces the incidence of dental cavities and help stop teeth decay (Harrison, 2005; Noh, 2005). Fluoride is attracted by positively charged calcium in teeth and bones due to its strong electronegativity (Kamble et al., 2007). Other reported diseases includes detrimental effects such as immunotoxicity, carcinogenicity, genotoxicity, reprotoxicity, teratogenicity, renal toxicity and gastrointestinal tract toxicity (Harrison, 2005).

Chloride is a corrosive agent and can be toxic to both aquatic life and plants. Elevated levels pose threat to infrastructures such as roadbeds, bridges and industrial pipes (Kelly et al., 2012; WHO, 2004a). However, there is no health-based guideline value that is proposed for chloride in drinking water (WHO, 2008). Although, excess concentration of chloride of about 250 mg L^{-1} give rise to detectable taste in water. The maximum allowable limit (MAL) of chloride is 250 mg L^{-1} (Canadian guideline, 2017). Water containing high amounts of chloride may be a threat to life especially if these water contain ammonia or organic matter that may convert chlorine to chloramines, which are less toxic but becomes toxic because of their persistency (Dikole M, 2014).

Nitrate is a primary drinking contaminant with the MAL of 10 mg L^{-1}, according to the U.S drinking water supplies and WHO (Glass and Silverstein, 1998; Organization, 2004). The incidence of methemoglobinemia resulted from a high nitrate concentration of greater than 10 mg L^{-1} (Ion, 2014). Methemoglobinemia or blue baby syndrome is a condition that limits the blood cells and their ability to carry oxygen and may be fatal to infants. High concentrations of nitrates in drinking water can prove to be deadly since it leads to the development of gastric and intestinal cancer. Nitrate is also good for the growth and reproduction of aquatic species. High use of nitrate may also lead to eutrophication (Dikole M, 2014).

Phosphorus is an essential element for all life including plant growth and photosynthesis in algae. Excess of phosphates input in natural water caused by over fertilisation of agricultural land and subsequent runoff lead to eutrophication, death of fish, growth of algae and many undesired effects (Serhii, 2015).

Sulphate is a commonly occurring anion in groundwater and surface water, where low concentrations (<5mg L^{-1}) of sulphate leads to the growth of algae, but if the sulphate concentration is greater than 500 mg L^{-1} this may lead to water tasting salty and causes pipe and fixture corrosion (NDEFO, 2008). Water containing high concentration of SO_4^{2-} greater than 250 mg L^{-1} lead to diarrhoea (Heizer et al., 1997). The average daily intake of sulphate from air on the assumption that 20 m^3 of air are inhaled daily would be in the range 0.02-0.63 mg (WHO, 2004b).

2.6.2 Health effects of cations

Consuming water containing high concentration of Aluminium causes neurological disorders such as alzheimer’s disease and dementia (Srinivasan et al., 1999; Flaten, 2001). The maximum permissible limit for Al in drinking water is 0.010 mg L^{-1} (SANS241, 2006). Exposure to excess calcium increases risks of osteoporosis, hypertension, stroke nephrolithiasis, stones risk (WHO, 2009). Calcium also has laxative effect with long time consumption (Samie et al., 2013a).

Vanadium compounds are toxic in high concentration or after a long period of exposure (Tavallali and Nejabat, 2015). The estimated daily intake of vanadium ranges from 6-18 µg (Wadhwa et al., 2013). According to environmental protection agency (EPA), permitted vanadium concentration level of drinking water is 50 mg L^{-1}. Vanadium (IV) has a detection limit of 0.02 µg L^{-1} and vanadium (V) detection limit of 0.06 µg L^{-1} in drinking water (Gamage et al., 2010). Vanadium exhibit chemotherapeutic effects in the treatment of leukaemia and recent studies showed promising application in managing diabetes (Khan et al., 2006). Excess vanadium causes cardiovascular disease, bronchitis, lung carcigema and paralysis. However, this trace element is also essential in the production of chlorophyll in plants and the growth of young animals, since it plays a role in regulation of enzymes, adenylate cyclase and protein kinases (Tavallali and Nejabat, 2015; Gamage et al., 2010).

Chromium compounds cause pneumonia and asthma if inhaled and when it comes to contact with the skin, they provoke allergies and dermatoses. Chromium is also carcinogenic and mutagenic for humans. Chromium (III) is essential to human trace concentration and is considered to be less toxic than Cr(VI). However, higher concentration of Cr(III) can cause adverse effects because of high capability of coordinating with various organic compounds, resulting inhabiting some metallic enzyme systems. According to European drinking water quality, the maximum allowable concentration of total chromium in drinking water is 50-10 µg L^{-1}. Tolerance limit for aqueous effluent discharge into inland waters is 1.0 mg L^{-1} for total Cr(III) and is 0.10 mg L^{-1} Cr(VI) (Ali et al., 2014). Chromium(VI) that is greater than 70 mg is very toxic, it causes cancer, asthma, nephritis and gastrointestinal ulceration (Martin and Griswold, 2009).

Copper sulphate is gastric irritant (Barceloux and Barceloux, 1999). Wilson's disease and Indian childhood cirrhosis are examples of severe chronic liver disease that results from the genetic predisposition to the hepatic accumulation of copper (Barceloux and Barceloux, 1999). Wilson’s disease is a rare autosomal recessive disorder of copper transport, resulting in copper accumulation and toxicity to the liver and brain (G. Georgopoulos, 2001). Infants and children under 1 year old are unusually susceptible to the toxicity of copper (G. Georgopoulos, 2001). Guideline value 2 mg L^{-1} (WHO, 2008). Guideline value for Zn in drinking water is 1.300 µg L^{-1} (Brima, 2017).

Arsenic is currently regarded as the most widespread naturally occurring and serious contaminant in drinking water (Ali, 2010). Arsenic is very mobile, it can accumulate in the keratin-rich tissues such as hair, skin or nails and also provoke cancers of the respiratory system, skin and organ (Melamed, 2005). The maximum contaminant level of arsenic in drinking water is 10 µg L^{-1} (Canadian guideline, 2017; SANS 241, 2006). Exposure to arsenic can cause health, dermal changes; respiratory, cardiovascular, gastrointestinal, genotoxic, mutagenic and cancer (lung, bladder, liver and skin) and neurological effects (Odiyo et al., 2005).

Consumption of water containing excess Cd level can accumulate in the kidneys, however, Cd has a long biological half-life of 1035 years in humans (Organization, 2008). Cadmium is known to affect several enzymes that causes proteinuria in the body (Wuana and Okieimen, 2011). Arsenic causes stomach irritation, vomiting, diarrhea, kidney disease, lung damage, and fragile bones (Martin and Griswold, 2009). According to WHO the maximum contaminant level of Cd in drinking water is 0.003 mg L^{-1} (WHO, 2008).

Thallium is one of the element that is highly toxic. Some of the thallium characteristic poisoning symptoms are hair loss followed by hair follicle atrophy, digestion disorders, pain, necropsy and cardiovascular system damage (Jabłońska-Czapla, 2015). It is considered one of the most toxic heavy metals causing both acute chronic and acute poisoning (Nagaraja et al., 2009). According to environmental protection agency (EPA), the maximum contaminant level of thallium in drinking water is 0.002 mg L^{-1}.

Lead in drinking water is a major public health concern. It can create irreversible intellectual impairment in infants and young children (Deshommes et al., 2010). Guidelines on the concentration of lead in drinking water are mostly in the range of 0.02 mg L^{-1} (SANS241, 2006). Other health effects are biochemical and neurobehavioral, blood pressure, anaemia, central nervous system effects and for children under the age of 6, it can affect their intellectual development, behaviour, size and hearing (Canadian guideline, 2017; Martin and Griswold, 2009).

2.7 Summary guideline tables of drinking water

Table (3 and 4) below shows the recommended MCL guideline set by WHO (2008), SANS 241 (2006), (Canada, 2017) and USEPA (2009) drinking water quality for anions and cations. These limits serve as health guideline for safe water drinking.

Table 2.3: Summary table of WHO, SANS and Canadian drinking water quality

Parameters	WHO (mg L^{-1})	SANS (mg L^{-1})	Canadian guideline (mg L^{-1})	USEPA (mg L^{-1})
Fluoride	1.5	1.0	1.5	4
Sulphate	≤500	<400	-	250
Chloride	≤250	<400	≤250	250
Nitrate	10.0	10.0	-	10
TDS	500.0	<1000	≤500	-
Arsenic	0.01	0.01	0.010	0.010
Aluminium	0.2	0.3	0.20	0.05-0.2
Cadmium	0.003	0.005	0.005	0.003
Chromium	0.05	<0.01	0.05	0.05
Copper	2.0	<1.0	≤1.0	0.0013
Lead	0.01	0.02	0.010	0.03
Magnesium	-	-	<70	-
Zinc	-	-	-	5
Sodium	≤200	<200	≤200	200
Uranium	≤0.015	-	0.02	-
Iron	50.0	<0.02	-	0.3
Calcium	200	-	-	-
Vanadium	-	<0.200	-	-
Nickel	-	<0.150	-	-
Cobalt	-	0.5	-	-
		Physico-chemical parameter		
pH	6.5-8.5	5-9.5	6.5-8.5	-

- Not reported

2.8 Techniques used for the determination anions and cations

Many analytical methods are widely used to determine the presence of contaminants in water such as excessive concentration of anions and cations. There are many reported techniques used for the analysis of anions and cations. However, commonly used techniques in the industry and academic world are the graphite flame atomic absorption spectroscopy (GFAAS), ion chromatography (IC), inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma-optical emission spectrometer (ICP-OES). The IC, ICP-MS and ICP-OES were the techniques used for the project. They were chosen based on the sensitivity and because they are multi elemental analysis instrument.

2.8.1 Principles of IC technique

According to Jackson (2000), IC is considered a technique which can be used for the determination of the ionic solutes, inorganic anions, inorganic cations such as alkali metal, alkaline earth, transition metal. Ion chromatography separates ions using a solid ion exchange resin, conductivity detector and a column. The determination of anions usually has a mixture of carbonated species and hydrogenated strong cation resin. The following separation principles apply in ion chromatography: ion exchange, ion pair formation and ion exclusion. The analyte passes through a degasser, followed by a pulse dampener, a guard column, and the analytical column. After the analytical separation occurs, the eluent passes through the suppressor, which is full of H^+ ions that diffuse into the eluent and neutralize ions in the mobile phase, then signal is produced by the conductivity (Haddad and Jackson PE, 1990).

2.8.2 Principle of ICP-OES technique

Inductively coupled plasma optical emission spectrometry (ICP-OES) also determines alkali and alkali earth elements. The principle of operation includes, a sample introduction system, which receives a sample at a constant rate to the ICP emission source (plasma), where desolvation, atomization, excitation and light emission occur (Abegaz, 2005). During the excitation process, atomic and ionic species in various energy stages are produced. Energy is released in the form of electromagnetic radiation and, as a result, a wavelength is formed, which is characteristic of the emitting species (Charles and Fredeen, 1997). Components of the ICP-OES instrument include the peristaltic pump, the nebuliser, the spray chamber, the (radio frequency) rf generator, the torch, the optical systems, the detectors and the data processing system.

2.8.3 Principle of ICP-MS technique

ICP-MS is a multi-elemental analysis with an excellent sensitivity and can perform qualitative, semi-quantitative and quantitative analysis, and with the assistance of the mass analyzer, it therefore measures isotopic ratios (Abegaz, 2005). The principle of operation for ICP-MS includes a sample introduction system, which supplies sample at a constant rate to the ICP emission source (plasma). ICP-MS the plasma is used to generate positively charged ions (Wolf, 2005). Once the ions are present in the plasma, they are projected through a low vacuum interface into the mass spectrometer chamber and focused via an ion lens system onto a quadrupole mass filter. The interface region consists of two metallic cones (usually nickel), called the sampler and skimmer cones which allow the ions to pass through to the ion optics. Ions which reach the quadropole are separated based on their mass to charge ratio, interfering and matrix ions. The last step is to convert the ions into an electrical signal with a dynode detector.

2.8.4 Limit of instrumental detection limit of selected parameters

Table 2.4: Limit of detection for selected parameters

Parameter	Method	Detection limit	Unit	References
F^-	IC	0.01	mg L^{-1}	(WHO, 2008)
	ISE	0.1	mg L^{-1}	(WHO, 2008)
NO_3^-	IC	22.0	µg L^{-1}	(WHO, 2008)
	LC	0.1	mg L^{-1}	(WHO, 2008)
Al	GFAAS	0.2	µg L^{-1}	(Abegaz, 2005)
Cr	ICP-MS	0.02	µg L^{-1}	**(**WHO, 2008)
	AAS	0.05-0.2	µg L^{-1}	(WHO, 2008)
Co	ICP-MS	0.009	µg L^{-1}	(Abegaz, 2005)
Ni	ICP-MS	0.1	µg L^{-1}	(WHO, 2008)
	ICP-AES	10	µg L^{-1}	(WHO, 2008)
	FAAS	0.5	µg L^{-1}	(WHO, 2008)
Cu	ICP-MS	0.02-0.1	µg L^{-1}	(WHO, 2008)
	ICP-OES	0.3	µg L^{-1}	(WHO, 2008)
	FAAS	0.5	µg L^{-1}	(Abegaz, 2005)
Zn	ICP-MS	0.003	µg L^{-1}	(Abegaz, 2005)
As	GFAAS	0.25	µg L^{-1}	(Abegaz, 2005)
	ICP-MS	0.1	µg L^{-1}	(WHO, 2008)
	ICP-AES	2.0	µg L^{-1}	(WHO, 2008)
Mo	GFAAS	0.25	µg L^{-1}	(WHO, 2008)
	ICP-AES	2	µg L^{-1}	(WHO, 2008)
Cd	ICP-MS	0.003	µg L^{-1}	(Abegaz, 2005)
	ICP-MS	0.01	µg L^{-1}	(Abegaz, 2005)
Pb	GFAAS	0.2	µg L^{-1}	(Abegaz, 2005)
	ICP-MS	0.001	µg L	(Abegaz, 2005)

2.9 Water sampling methods

Traditional method: This method has been widely used by researchers and even today, it is still being used. Traditional methods such as grab method require the transport of large quantities of water from sampling places to laboratory (Vrana et al., 2005), followed by extraction and instrumental analysis. Samples are often collected by direct filling of the sampling bottle. However, for deep water this method cannot be used thus the use of pumps (peristaltic pumps offer the option of collecting larger amounts of water) can implemented (Madrid and Zayas, 2007).

Passive-sampling Method: The passive samplers is becoming more and more popular these days, especially in determining analysis at trace concentration (Pogorzelec and Piekarska, 2017). Passive sampling method is based on free flow of analyte molecules from the sampled medium to a receiving phase in a sampling device (Vrana et al, 2005). The net flow of analyte from one medium to the other continues until equilibrium is established. The main reason for using passive sampling is that it measures exactly what is needed for risk assessment, namely the freely dissolved concentration of a substance. This freely dissolved concentration is proportional to the chemical activity of the compound, which has been known to determine the risk for organisms for a long time (Mayer and Reichenberg, 2006). Passive methods are classified as adsorptive or absorptive (Kot et al., 2000). It can be used for the determination of both inorganic and organic compounds in a variety of matrices, including air, water and soil. Examples of passive samplers are semi-permeable membrane devices (SPMDs), Diffusion-gradient in thin-films (DGTs) and polar organic chemical integrative samplers (POCIS). Passive sampling takes into account, the analyte concentration, flow rate, time, and deployment period.

Chapter 3: Experimental details

This section will describe the area of the study, al materials, reagents and analytical techniques used for the study. It also gives a description on how samples were collected and how standards were prepared.

3.1 Study area and sampling sites

Samples were collected from four sites around Musina area: (Mutale river, Nwanedi river, Tshipise river and Nzhelele river. These four sampling points are located in Vhembe district, North of Limpopo province. The sampling points are displayed in Figure 3.1 and the GPS coordinates of the sampling points are described in Table 3.1. Mutale river is located very close to Tshikondeni mine (coal mine) about 16.6 km away. The community in the area practice subsistence and commercial farming, they also use water for irrigation, drinking, washing and as well as bathing. Nwanedi river is a tributary of the Limpopo river flowing east of the Nzhelele. There are a lot of plantations and farming happening around the river and the community use Nwanedi river water for irrigation. Tshipise river is also situated close to the community, this river is used for drinking by animals and irrigation. Nzhelele river is situated in the far north of Louis Trichardt. Community uses the water from this river for washing, drinking and fishing. According to Edokpayi et al. (2017), Nzhelele river catchment area is 2, 436 km^2 and receives effluents from the Siloam waste stabilization ponds (WSPs). Furthermore, the study area is semi-arid with a shortage of potable water supplies thus the community using water for subsistence agriculture and domestic use.

Table 3.1: GPS coordinates of the sampling points

Sites	Latitudes (N)	Longitude (E)
Mutale river	22° 32' 24.360’’ N	30° 28' 15.5964’’E
Nwanedi river	22°28’60’’N	30° 49’0’’E
Tshipise river	22° 52'43.5828" N	30° 6' 58.1904’’ E
Nzhelele river	22°27’0’’N	31°4’60’’E

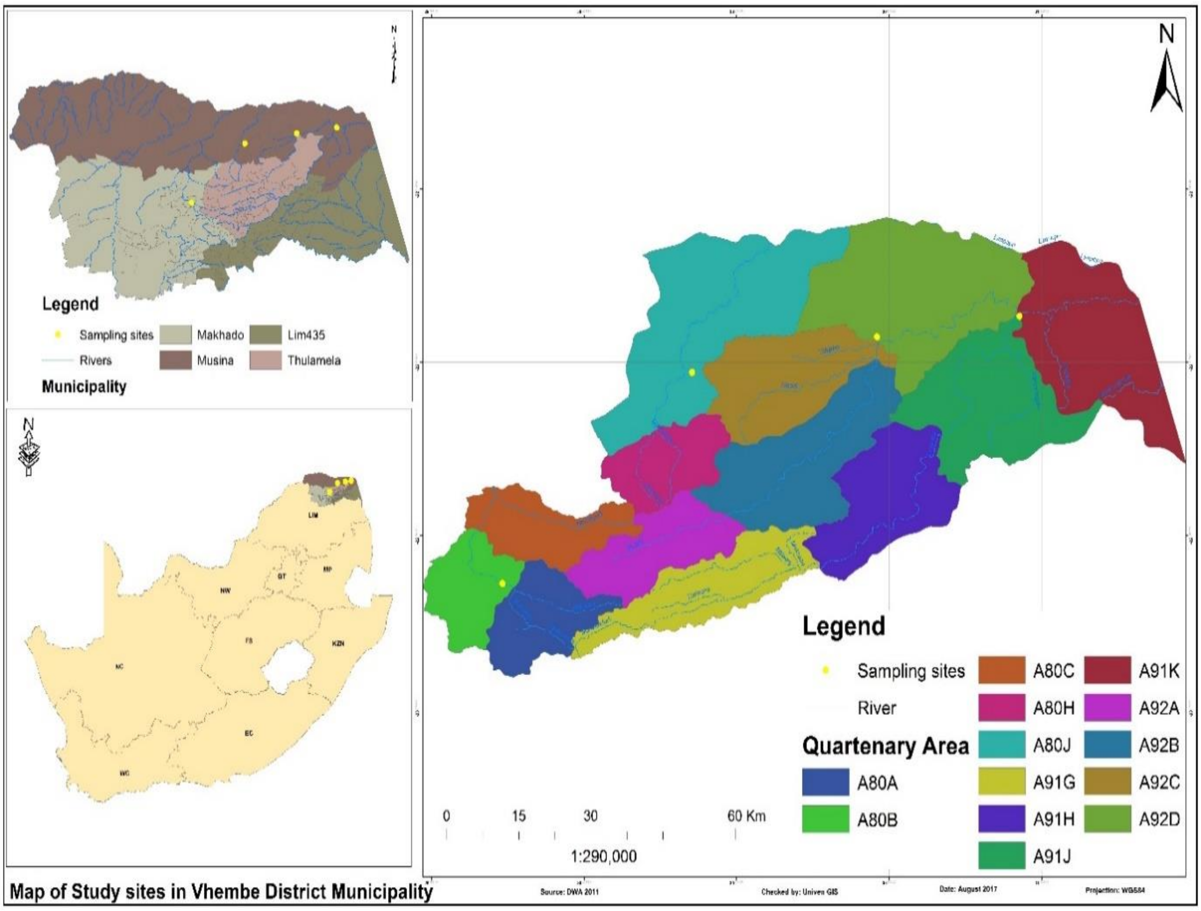

Figure 3.1: A map of specific study sites in Vhembe district.

3.2 Methods

3.2.1 Sample collection and sample preparation

3.2.1.1 River water samples

Water samples were collected from four rivers, namely: Mutale river (N=4), Nwanedi river (N=3), Tshipise river (N=1) and Nzhelele river (N=2), during rainy (April 2017) and dry season (July 2017) by using grab method. Samples for the determination of anions were collected in 500 mL sampling bottles and samples for the determination of cations were preserved with two drops of 55% (v/v) HNO_3. All bottles and filtration apparatus were previously washed with 10% (v/v) HNO_3 and rinsed thoroughly with deionised water. All samples were stored at 4°C in the fridge prior to analyses. Dissolved and particulate matters in the water samples were filtered through a cellulose membrane filter having 0.45 µm pore size before analyses. Figure 3.2 and 3.3 shows examples of pictures taken by the author from the sampling sites.

Figure 3.2: People fetching water and washing their clothes in Mutale river

Figure 3.3: Nwanedi river being used for the purpose of irrigation

3.2.1.2 Soil samples

Four soil samples were collected at approximately 30 metres away from the river sampling sites. The samples were collected once during rainy season in April 2017. Approximately 500g of soil was collected from 0-30 cm depth by using a stick and transferred into plastics and stored in the cupboard until analysis.

3.2.2 Materials and reagents

Eluent Solution**:** A mass of 0.168 g dried Sodium hydrogen carbonate from Minema (JHB, SA) was diluted in 2L volumetric flasks to make 1.0 mmol L^{-1} eluent. About 0.678 g of sodium carbonate from Minema (JHB, SA) was also prepared in a 2L volumetric flasks with deionised water (miliQ water purification system, Millipore, Belford, MA, USA) to make 3.2 mmol L^{-1} eluent. The eluent was then degassed with nitrogen gas for more than ten minutes. About 0.05 M Sulphuric acid from Merck (JHB, SA) was prepared with deionised water to use as part of the reagents. Suprapur grade nitric acid (HNO_3) was bought from (Merck, Darmstadt, Germany) to use for acidification. Multi-anion Standard Solution, containing 1000 mg L^{-1}, F^-, $Cl^{\ -}$, Br^-, $NO3^-$, $SO4^{2-}$, and $PO4^{3-}$ was used to make IC standards and working standards (Merck, Demarstat, Germany). Multi-elemental ICP standard solutions containing 1000 mg L^{-1} bought from (Merck, Darmstadt, Germany) was used to make calibrations for the following elements (Al, Ca, Fe, K, Mg and Na) and (Li, V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, Tl and Pb) in 1 % (v/v) HNO_3 acid.

3.2.3 Preparation of stock and standard solution

Standards for IC analysis: An amount of 10 mL of 1000 mg L^{-1} multi-anion standards was mixed with deionised water to make a standard solution of 100 mg L^{-1} containing F^-, Cl^-, Br^-, NO_3^-, SO_4^{2-} and PO_4^{3-}. Then 100 mg L^{-1} standard was used to make other preceding standards with a concentration of 10, 20, 30, 40, 50, 60 and 70 mg L^{-1}. The instrument was then calibrated by using these standards to obtain a calibration curve. Seven chromatograms of the respective standards containing peaks of all anions were obtained and five calibration curves of each anion (F^-, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}) were then obtained.

Calibration standards for ICP-OES determination: Calibration standards for ICP-OES analysis were prepared by diluting commercially available 1000 mg L^{-1} stock solutions of selected elements (Al, Ca, Fe, K, Mg and Na) in 1 % (v/v) HNO_3 acid. From the stock solution, calibration standards of 1, 5, 10, 20, 40, 80 and 100 mg L^{-1} were prepared with an appropriate matrix matching to the samples using 1 % (v/v). Argon was selected as a monitor for verification of matrix effects between samples and calibration standards.

Calibration standards for ICP-MS determination: Calibration standards for ICP-MS analysis were prepared from commercially available 1000 mg L^{-1} stock solutions of selected metals (Li, V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, Tl and Pb) in 1 % (v/v) HNO_3 acid. A second stock solution (10 mg L^{-1}) was then prepared in 1% HNO_3 acid. An additional calibration stock solution (third stock) of 100 µg L^{-1} was prepared in 1 % HNO_3. Calibration standards of 0.5, 1, 5, 10 and 20 µg L^{-1} were prepared from the third stock solution and appropriately matrix-matched to the samples using 1 % of HNO_3 acid. Internal standard (Ga, 10 µg L^{-1}) was included in both samples and calibration standards.

3.2.4 Quality control measures

Quality control for ICP-OES analysis: Involved the preparation of the following fresh standards: Initial calibration blank (ICB) of 1 % (v/v) HNO_3 acid, 1 mg L^{-1} of initial calibration verification standard (ICV) and continuing calibration blank (CCB) run every 10 samples to ensure no memory effects. Continuing calibration verification standard (CCV) run every 10 samples to ensure that calibration was still within specification (1 mg L^{-1}). Quality control standard (QCS), higher calibration verification standard to ensure that upper range of calibration was still within specification (80 mg L^{-1}). The internal standard was monitored and found to lie within the required 65-125 % limit as set out by the USEP, thus indicating no major matrix effects.

Quality control for ICP-MS analysis: Quality control involved the preparation of the following fresh standards: ICB: initial calibration blank (1 % HNO_3) and ICV (1 µg L^{-1}). CCB was ran for every 10 samples to ensure no memory effects, CCV standard run every 10 samples to ensure that calibration was still within specification (1 µg L^{-1}). QCS and higher calibration verification standard to ensure that upper range of calibration was still within specification (15 µg L^{-1}). The internal standard (Ga, 10 µg L^{-1}) was monitored and found to range from 65-125 % limit as set out by the USEP, thus indicating no major matrix effects.

3.3 Analytical methods

3.3.1. Physico-chemical parameters

The following parameters: pH, temperature, EC and TDS were investigated in all the river samples. Temperature of the river samples were recorded at the sampling site using a thermometer. pH and EC were analysed in the laboratory immediately after samples were collected by using pH meter (Bante 900p, Shangai, China) and bench ISE/pH meter Lasec (JHB, SA). The pH electrode was calibrated before analyses with 4.1, 7.2 and 9.1 buffer solution. The EC was calibrated with 1413 ms cm^{-1} standard solution. TDS was also determined through the conversion of EC by using the equation: TDS = 0.64 X EC.

3.3.2 Soil samples analysis

Soil samples were collected near sampling areas (Mutale river, Nwanedi river, Tshipise river and Nzhelele river). Samples were analyzed for Cr, Mg, Al, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As and Tl content. The instrument used for the analysis of soil sample was XRF (Rigaku NEX model). Soil samples were pulverised to a fine powder using the Retsch Grinding mill and compressed using the Pana Press machine for 1 minute, at 300 inches per pound.

3.3.3 IC analysis

Analysis of anions (F^-, Cl^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) were performed on a Metrohm 850 professional IC from (Switzerland, Herisau). The samples were filtered through 0.45-micron syringe filter and placed in an autosampler connected to an 850 professional IC. A volume of 20 µL sample was introduced into an autosampler where anions of interest were separated and measured within 20 min interval each through the column (Metro A Supp 5-100/4.0 (6.10006.510)). The operational conditions used for the IC analysis were as follows: flow rate of 0.7 mL min^{-1}, temperature of 30° c, maximum and minimum pressure of 15.0 MPa and 0.1 MPa, respectively. Samples and standards were analysed in triplicate. Then chromatograms of each sample were obtained and all the concentrations of each anion were recorded.

3.3.4 ICP-OES analysis

The concentration of selected elements (Al, Ca, Fe, K, Mg, and Na) were analysed using Spectro ARCOS ICP-OES (Cleve, Germany) with radial plasma view. The spectrometer was equipped with Cetac ASX- 520 auto-sampler, cross-flow nebulizer and double pass Scott type spray chamber. Humidifier and extensive rinsing was used to reduce high TDS caused by sodium. The optimal operating conditions used for ICP-OES analysis were as follows: radio frequency generator power (1400 W), pump speed (30 rpm), plasma gas flow rate (13 L min^{-1}), auxiliary flow rate (2 L min^{-1}) and nebulizer flow rate (0.95 L min^{-1}). The solution uptake rate was 2.0 mL min^{-1} and the integration time was 12 seconds. Standards were prepared for working concentrations of (1, 5, 10, 20, 40, 80 and 100 mg L^{-1}). Concentrations of samples were monitored at different possible emission lines: Al (396.152 nm), Ca (317.933 nm), Fe (239.562nm), K (766.491nm), Mg (285.213 nm) and Na (589.592 nm) respectively.

3.3.5 ICP-MS analysis

The concentration levels of selected trace metals (Li, V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, Tl and Pb) were measured using Perkin-Elmer NexION 300 ICP-MS Spectrometer (USA, Shelton, CT) with a triple cone interface (which allows for less spread of the ions, photons and neutrals as they get transferred into the ion optics), two modes of operation (collision and standard modes) and a single quadrupole was used throughout the analysis. The spectrometer was fitted with a Perkin-Elmer S10 autosampler. During elemental measurement, a concentric type quartz nebulizer, quartz spray chamber, quartz injector, nickel cones (sampler and skimmer) and aluminium hyper skimmer with cone gasket were utilized. The operating conditions used for ICP-MS spectrometer during the measurements were as follows: forward power: 1500 W, plasma argon flow rate: 18 L min^{-1}, auxiliary argon flow rate: 1.0 L min^{-1} and nebulizer argon flow rate: 0.95 L min^{-1}.

Chapter 4: Results and discussion

This chapter gives a discussion on the experimental results. The first section (4.1) describes the quality control data whereas Section (4.2) describes the results of metals obtained from soil samples, and section (4.3) determines and discusses the experimental data of anions and cations by using IC, ICP-OES and ICP-MS for selected trace metals.

4.1 Quality control data

4.1.1 Calibration data for IC analysis

4.1.1.1 Calibration curves of IC standards

The calibration curve was constructed using standard solutions ranging from 10-70 mg L^{-1}. The calibration curves in Figure 4.1 were obtained from the multi-elemental standards. The concentrations of the standards were determined from three replicate injection of an analyte. The method of linearity was obtained from seven calibration standards and resulting linear correlation coefficients of determination (R^2). Retention time and peak area in Table 4.1 is expressed in RSD. The repeatability was evaluated by examining the RSD of the retention times for 3 injections set at seven different concentration levels, in the 10-70 mg L^{-1} concentration range, which thus shows that the separation was achieved. All the RSD’s for the peak retention time were below 5 %. Therefore, gives rise to good calibration and good separation of the anions peaks. The equation and the coefficient of determinations obtained for the calibration curves are also listed in Tables 4.1. The R^2 of all the anions standards were ranging from 0.937-0.9997, showing that the method is suitable for the determination of anions. Tables 4.1 shows typical retention time and peak area precision data that can be obtained from inorganic anions using Sup-Metrom A of the ion chromatography N=7.

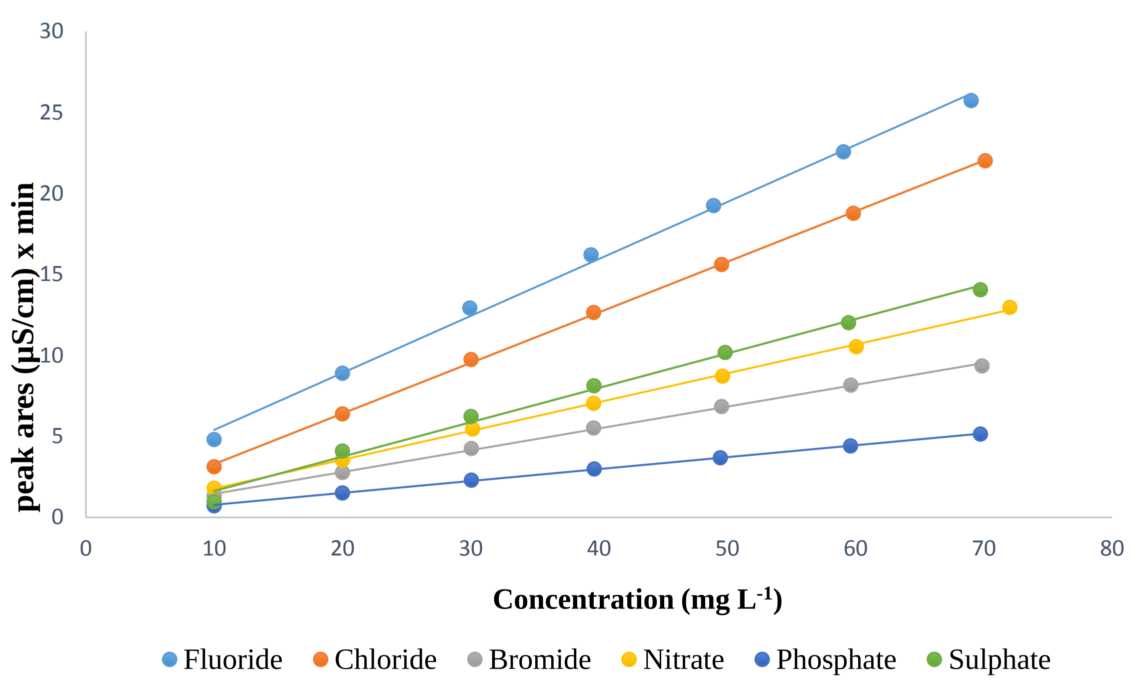

Figure 4.1: Calibration curves of anions standards generated from linear range data (10 to 70 mg L^{-1}) rainy season analysis

Table 4.1: Correlation coefficient, retention time, linearity equations obtained by using ion chromatography

Anion	Correlation coefficient (R^2)	Linearity equation	Retention time (RSD)	Peak area precision (RSD)
Fluoride	0.9969	Y=0.358x +1.8844	0.0291	6.9002
Chloride	0.9997	Y=0.3122x+0.1685	0.0205	6.2345
Bromide	0.9937	Y=0.214x-0.4987	0.0035	2.6771
Nitrate	0.9993	Y=0.1779x-0.0001	0.0049	3.6330
Phosphate	0.9988	Y=0.1346x+0.1091	0.0083	1.4602
Sulphate	0.9994	Y=0.0736x+0.0400	0.0261	4.0016

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4.1.1.2 Chromatogram of standards

Figures 4.2 and 4.3 show selected IC chromatograms of anion standards containing concentrations (10 and 70 mg L^{-1}) of anions separated by using Metro A Supp 5-100/4.0 (6.10006.510) column. These chromatograms were obtained from three times injection of multi-standard composed of fluoride, chloride, bromide, nitrate, phosphate and sulphate anions. Seven chromatograms with six anions peaks were obtain and eluted at different retention times. All anions were well resolved within a total retention time of less than 18 min. Moreover, Figure 4.2 shows a chromatogram of 10 mg L^{-1} and Figure 4.3 shows a 70 mg L^{-1} chromatogram of a standard.

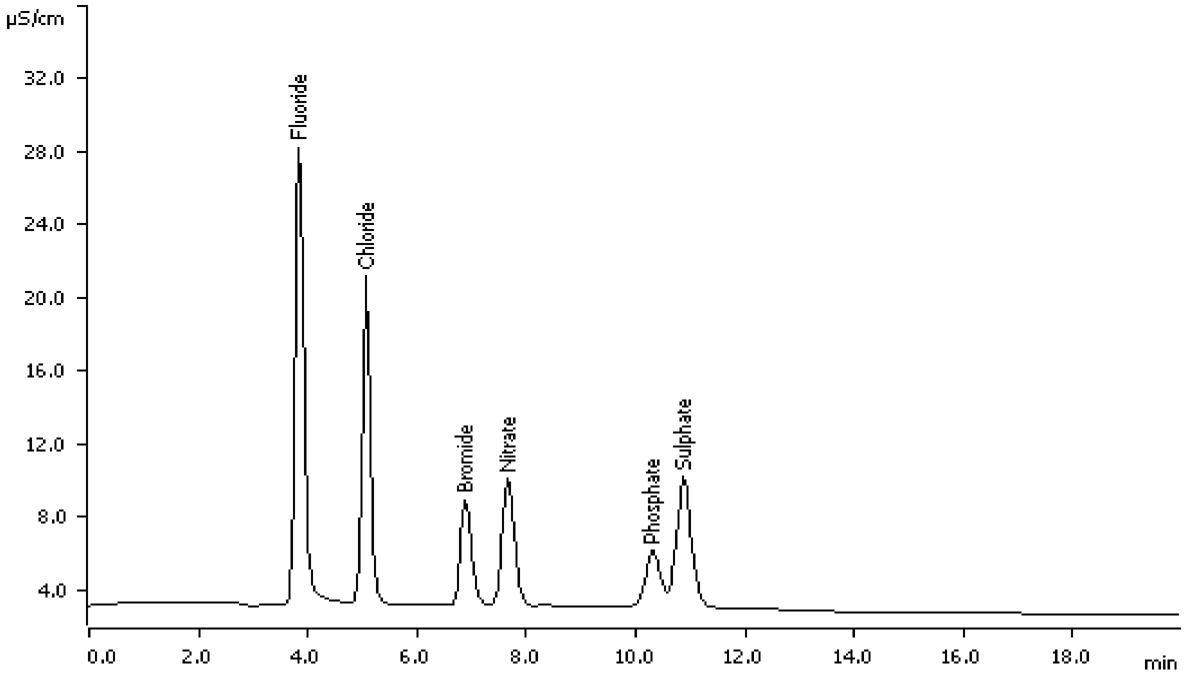

Figure 4.2: 10 mg L^{-1} chromatogram

Chromatogram with the following concentration: F^- =10.00 mg L^{-1}, Cl^- =10.00 mg L^{-1}, Br^- =10 mg L^{-1}, NO_3^- =10.00 mg L^{-1}, PO_4^{3-} = 10.00 and SO_4^{2-} = 10.00 mg L^{-1}.

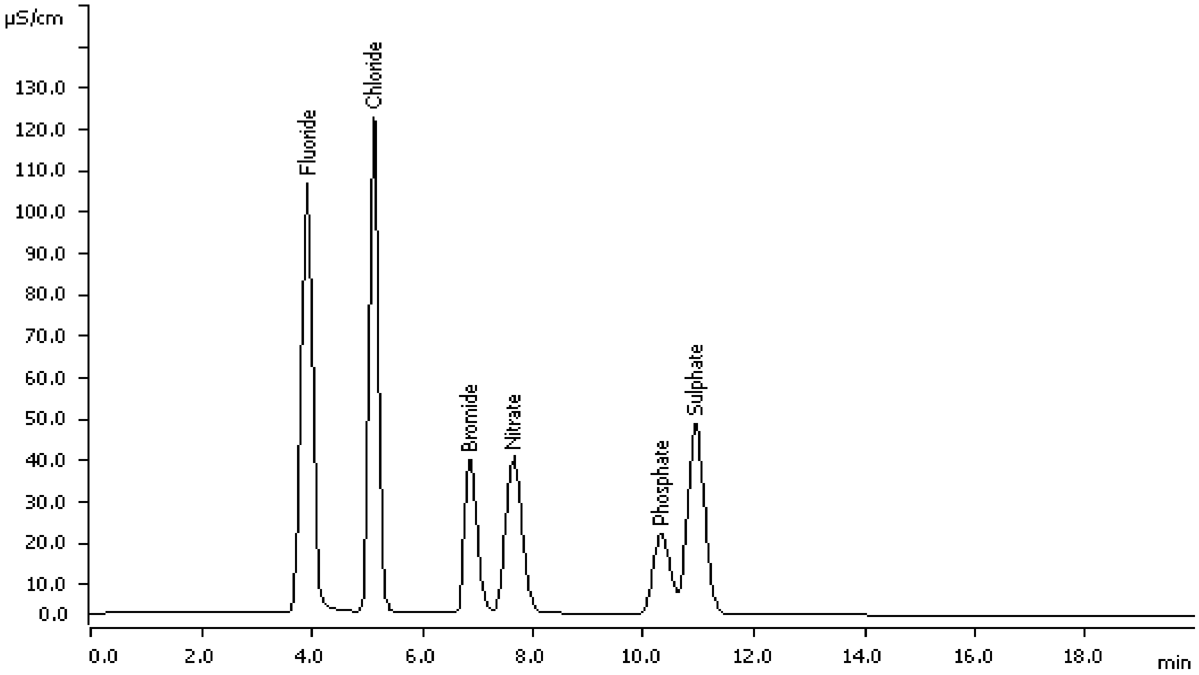

Figure 4.3: 70 mg L^{-1} Chromatogram

Chromatogram with the preceding concentration F^- = 68.94 mg L^{-1}, Cl^- = 70.11 mg L^{-1}, NO_3^- = 69.85 mg L^{-1}, Br^- = 69.850 mg L^{-1}, PO_4^{3-} =72.03 and SO_4^{2-} = 69.728 mg L^{-1}.

4.1.1.3 Chromatogram of samples

Figures 4.4 and 4.5 show chromatograms of samples with the peaks of interest, elution order and their respective retention times. Chromatogram in Figures 4.4 and 4.5 show results of samples obtained from Mutale and Nwanedi river. Figure 4.5 had high concentration of chloride and sulphate. The chromatogram in Figure 4.4 shows five eluted peaks from the Mutale river sample with the average concentration: F^- <1 mg L^{-1}, Cl^- = 9.282 mg L^{-1}, Br^- <1, NO_3^- = 6.265 mg L^{-1} and SO_4^{2-} = 1.549 mg L^{-1}. Figure 4.5 also shows separation of five eluted peaks obtained from Tshipise river sample with the average concentrations of F^- = 6.403 mg L^{-1}, Cl^- = 962.495 mg L^{-1}, Br^- <1 mg L^{-1}, NO_3^- = 0.747 mg L^{-1} and SO_4^{2-} = 289.657 mg L^{-1}.

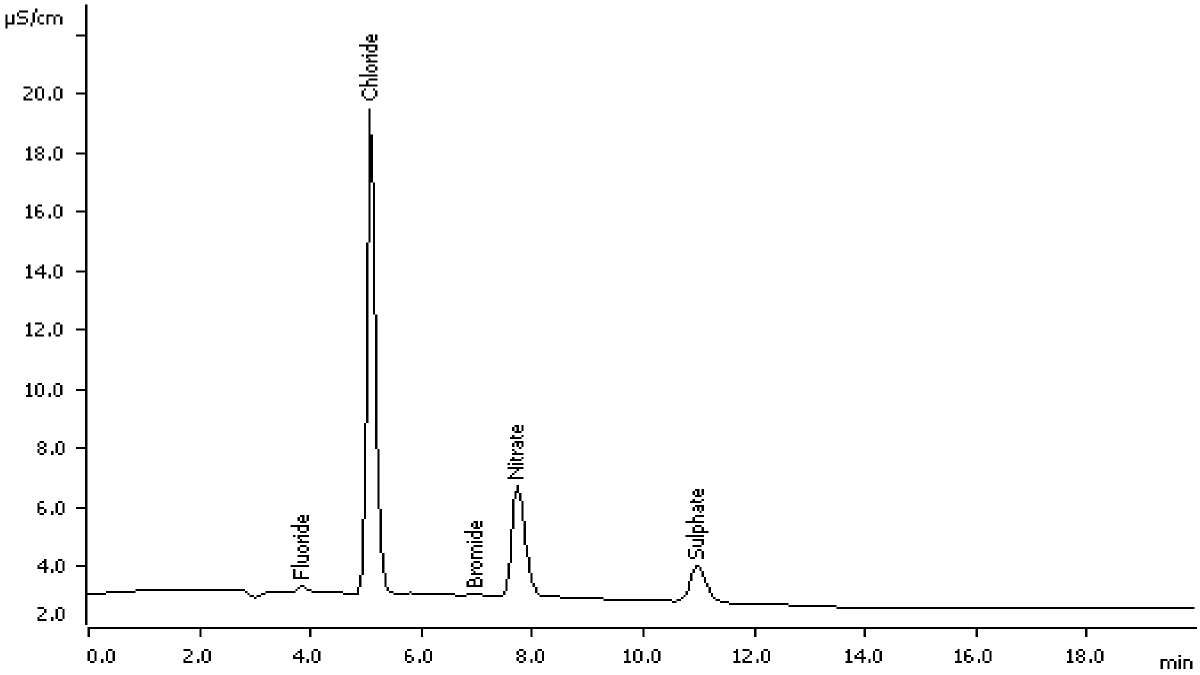

Figure 4.4: Chromatogram of Mutale river sample (rainy season)

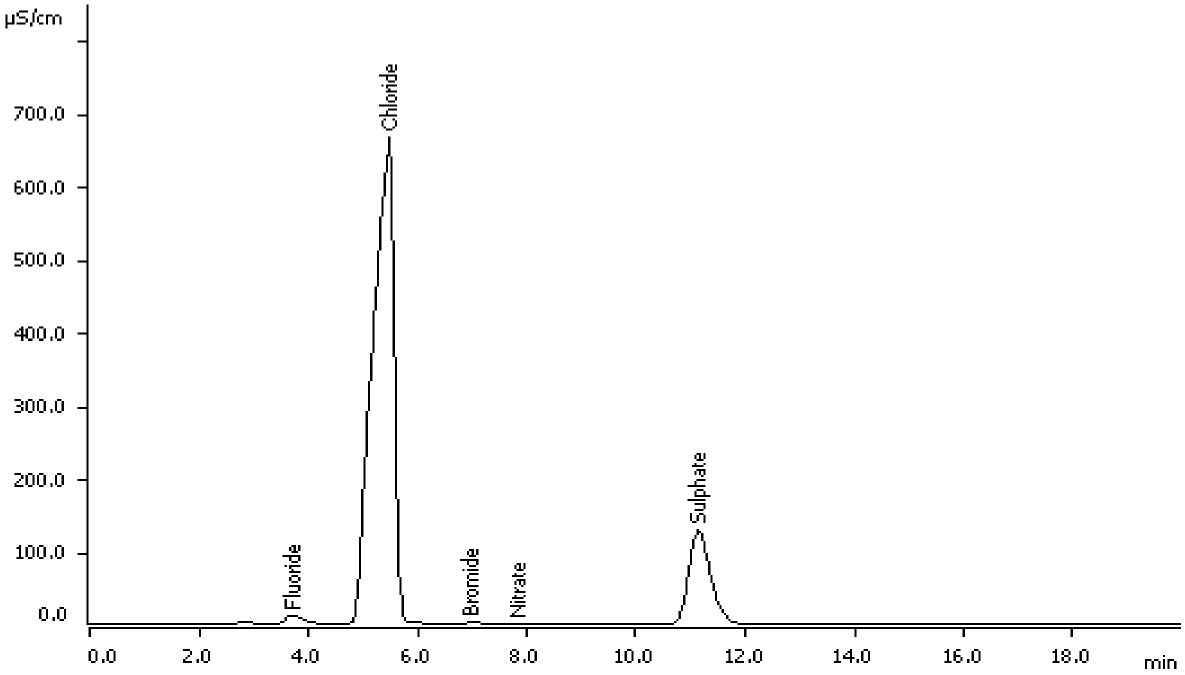

Figure 4.5: Chromatogram of Tshipise river sample 8 (dry season)

4.1.2 Calibration data for ICP-OES analysis

4.1.2.1 Calibration of ICP-OES standards

The instrument was calibrated using the following standard solutions 1, 5, 10, 20, 40, 80 and 100 mg L^{-1}. Table 4.2 below, shows calibration information of selected elements. The method of linearity was obtained from seven calibration standards and resulting linear coefficients of determination (R^2). The R^2 of all the selected cations standards were > 0.999, displaying that the method is suitable for the determination of cations. The lowest correlation coefficient was observed from Na, whilst, the highest was from Al. Three operational blanks were run to determine the limits of detection (LOQ = 3 × SD), and three replicates were used for limits of quantification (LOD = 10 × SD).

Table 4.2: Calibration information of selected wavelength lines (nm) from the ICP-OES analysis

Analytes	Wavelength (nm)	Limit of detection mg L^{-1}	Limit of quantification mg L^{-1}	Correlation coefficient (R^2)
Al	396.152	0.002940	0.00980	0.99999
Ca	317.933	0.002820	0.00940	0.99994
Fe	239.562	0.007120	0.02370	0.99978
K	766.491	0.001950	0.00650	0.99985
Mg	285.213	0.000559	0.00190	0.99992
Na	589.592	0.002870	0.00960	0.99974

4.1.2.2 Quality assurance of ICP-OES analysis

Five samples of the certified reference material (CRM) LGC6019 for Al, Ca, Fe, K, Mg and Na were run after the 10 operational blanks for quality assurance (QA) purposes. From the concentration of CRM (mg L^{-1}) and measured concentration (mean ± SD**)**, 95 % confidence interval, % recovery and % relative standard deviation (% RSD) were obtained (Table 4.3). The recoveries shown in Table 4.3 ranged from 73-104 %, which shows that the percentage of analytes recovered, were good.

Table 4.3: Accuracy (% recovery) and precision (% RSD) of ICP-OES analysis for quality assurance using river water certified reference material (LGC6019), n=5

Analytes	CRM concentration (mg L^{-1})	95% Confidence interval	Measured concentration (mg L^{-1})	Repeatability (%RSD)	Percentage recovery (%)
Al	0.073	0.013	0.053±0.000752	0.99999	73
Ca	109.000	3.000	114±0.600891	0.99994	105
Fe	0.287	0.007	0.299±0.002463	0.99978	104
K	4.780	0.120	4.55±0.074541	0.99985	95
Mg	4.620	0.120	4.26±0.015503	0.99992	92
Na	24.700	0.500	25.5±0.112067	0.99974	103

4.1.3 Calibration of ICP-MS analysis

4.1.3.1 Calibrations of standards for ICP-MS

The calibration standards were prepared using standard solutions of 0.5, 1, 5, 10 and 20 µg L^{-1}. Table 4.4 below shows calibration of trace metals from the ICP-MS analysis. The method of linearity was obtained from seven calibration range and resulting linear coefficients of determination (R^2). The correlation coefficient of all the selected cations standards were >0.999, showing that the method is suitable for the determination of cations. Three operational blanks were ran to determine the limits of detection (LOQ = 3 × SD), and three replicates were used for limits of quantification (LOD = 10 × SD).

Table 4.4: Calibration of trace metals from the ICP-MS analysis

Analyte	Limit of detection ($\mu g\ L^{-1}$)	Limit of quantification ($\mu g\ L^{-1}$)	Correlation coefficient (R^2)
Li	0.42091	1.40302	0.99972
V	0.19748	0.65827	0.99994
Cr	0.46784	1.55946	0.99977
Co	0.16378	0.54593	0.99996
Ni	0.24536	0.81786	0.99991
Cu	0.55039	1.83464	0.99968
Zn	0.75186	2.50619	0.99911
As	0.17124	0.57081	0.99995
Mo	0.11803	0.39344	0.99998
Cd	0.04367	0.14556	0.99999
Tl	0.27437	0.91456	0.99988
Pb	0.53949	1.79832	0.99954

4.1.3.2 Quality assurance for ICP-MS analysis

Table 4.5 shows the percentage accuracy and the precision of analysis using river water certified reference material. The accuracy is expressed as percentage recovery and precision is expressed by repeatability. The recoveries shown in Table 4.5 ranged from ND-112 %. The % RSD for all trace element were below 5%. Samples of the certified reference material (LGC6019) were ran after the 10 operational blanks for quality assurance (QA) purposes.

Table 4.5: Accuracy (% recovery) and precision (% RSD) of ICP-MS analysis for quality assurance using river water certified reference material (LGC6019), n = 5

Analyte	CRM concentration (µg L^{-1})	95% Confidence interval	Measured concentration (µg L^{-1})	Repeatability (%RSD)	Percentage Recovery (%)
Li	NC	NC	5.236±0.075	1.432	ND
V	NC	NC	0.544±0.006	1.104	ND
Cr	0.780	0.20	0.755±0.010	1.258	97
Co	NC	NC	0.597±0.0075	1.257	ND
Ni	NC	NC	2.505±0.053	2.100	ND
Cu	15.400	1.50	14.568±0.107	0.735	95
Zn	59.700	2.50	55.886±0.823	1.472	94
As	NC	NC	1.156±0.014	1.228	ND
Mo	NC	NC	0.916±0.013	1.452	ND
Cd	NC	NC	0.322±0.013	4.009	ND
Tl	NC	NC	<DL	ND	ND
Pb	5.200	0.30	5.865±0.122	2.085	112

NC = Not certified, ND = Not detected, DL = Detection limit

4.2 Determination of metals in soil samples

Trace elements in an agro-ecosystem are either inherited from soil parent materials or inputs through human activities (He et al., 2005). Continuous use of metal-enriched chemicals, fertilizers, manures and sewage sludge may cause contamination at a large scale as they are washed and deposited in the water bodies (He et al., 2005). Water containing toxic substances degrade the water for domestic, industry, recreation and agriculture use. The following trace elements (Cu, Zn, Fe, Mo, Co, Ni, Pb, Cd, Cr, As, Fe and Mo) have been extensively studied in the last decade, as they are essential for the growth of plants, health of animals and human beings. However, some of them are environmental concerning elements that have been reported to cause contamination in soil, water, and plants (Singare et al., 2012).

Table 4.6 shows the average concentration of heavy metals in soil samples obtained next to the rivers (Mutale, Nwanedi, Tshipise and Nzhelele river). The experimental data shows the average concentration (mg Kg^{-1}) of heavy metals such as Mg, Al, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As and Tl from the soil samples collected next to the river sampling points presented in Table 4.6. It was observed from the results that the average concentration of Al from different rivers ranged from (3.01-77749 mg Kg^{-1}), of which the lowest concentration was observed in Tshipise river and highest concentration was observed in Nwanedi river, Mutale river then Nzhelele river. The results have shown that the concentration of As from Mutale, Nwanedi, Tshipise and Nzhelele river were 1.594, 0, 0.0084, 25.5 mg Kg^{-1} respectively. It was also observed that the average concentration of Mg from the same sampling points was 0-495.381 mg Kg^{-1}. The results also indicated that Ca, V, Cr, Mn, Fe and Co had concentration ranging from 0.13-10595, 0.0018-102.5, 0.0562-192, 0.0455-1116.5, 2.4-287404 and 0.009-72.8 mg Kg^{-1} respectively. It was also observed that Ni, Cu, Zn, Al and Tl ranged from 0.0083-785, 0.0552-37.1, 0.030-37.1, 0.030-65.9, 0.0084-4.16 and 0-0.958 mg Kg^{-1} respectively. The abundance of heavy metals in the soil samples were as follows Fe> Al> Ca > Mn> Zn > Cr> V> Co> Ni > As. Lower concentrations of metals were observed from Tshipise river. The reason for low concentrations may be caused by factors such as soil texture, organic matter and geographic make-up of the area.

Table 4.6: Average concentration of heavy metals in soil samples

Metals	Concentrations (mg Kg^{-1}) Mutale river	Nwanedi river	Tshipise river	Nzhelele River
Mg	-	-	-	495.381
Al	40289	77749	3.01	37002
Ca	1524	10595	0.13	5667
V	39.35	102.7	0.0018	50.3
Cr	40.5	192	0.0562	47.3
Mn	103.7	96.6206	0.0455	1116.5
Fe	8037	5487	2.4	287404
Co	45.6	72.8	0.009	67
Ni	35.3	78.5	0.0083	14.2
Cu	31.4	37.1	0.0552	19.5
Zn	65.9	63.5	0.0302	25.5
As	1.594	-	0.0084	4.16
Tl	-	-	-	0.958

- Not detected

4.3 Analysis of river water samples

4.3.1 Physico-chemical parameters

The results of the physico-chemical parameters are presented in Tables 4.7 and 4.8 for both dry and rainy season. The pH of all samples in Table 4.7 were around neutral and was within the recommended values of the WHO (2008), SANS 241 (2006) and Canadian guideline for drinking water quality. The pH values all samples obtained in rainy season ranged from 7.2-8.5. The pH values obtained are similar to those reported by Gilbert (2016). According to (Cheepi, 2012) water with 4.5-9.0 pH value can be used for irrigation. The temperature for all river samples in rainy season ranged from 19.1-20.5° C.

The higher the EC, the higher the TDS in river samples. The levels of TDS contributes to contamination of the aquatic system. The value of EC usually gives an indication of the presence of dissolved ions in water and the presence of these ions can alter the taste of water and also contribute to the hardness of water. Water with high EC values is not suitable for domestic purposes. From Table 4.7, the EC values obtained from different sampling points were different. The concentrations of TDS in Mutale samples (1-4) and Nzhelele (9-10) samples fall within WHO Standard guideline and was ranging from (46.5-100.8 mg L^{-1}) in rainy season (Table 2.3). However, higher TDS and EC were observed in Nwanedi samples and Tshipise sample. The EC and TDS values of Nwanedi and Tshipise river in Table 4.7 ranged from 696.0-5270 mS cm^{-1} and 445.4-3372.8 mg L^{-1} respectively. Nwanedi and Tshipise samples indicate that the water contains ions and salt. This means that water is not suitable for consumption and puts the community in danger of negative health effects such as diarrhoea, joint pains, skin allergies, gastrointestinal disturbances, and vomiting. The presence of high concentration of TDS could have been caused by excess application of ions containing fertilizers and pesticides on soils and runoff from naturally occurring salts containing rocks to surface water. The TDS results obtained in Tshipise river corresponds to the TDS values reported by Akan et al. (2010).

Table 4.8 shows the pH of the water samples in dry season ranged from 7.8-8.5, which indicates that, water is suitable for consumption. The and TDS values of Mutale, Nwanedi and Tshipise samples decreased in dry season, ranging from, 32.5-33.8 mg L^{-1}, 190.3-192.7 mg L^{-1} and 1864.0 mg L^{-1} respectively. Only samples from Nzhelele river, showed an increase of TDS and EC values in dry season. However, Tshipise river recorded higher EC and TDS values that exceeded the recommended values for domestic water use (Table 2.3). The TDS of Mutale (1-4) and Nzhelele (9-10) samples were in line with what Jonnalagadda and Mhere (2001) reported. The EC for all samples were below the recommended values (Table 4.8) except for sample 8, which contained elevated values of EC in dry season. Hence, water may not be suitable for domestic and agricultural use.

Table 4.7: Physico-chemical parameters of samples obtained in rainy season

Sample site	Sample name	pH	Temperature (◦ c)	EC (mS cm^{-1})	TDS (mg L^{-1})
Mutale river	1	7.9	20.3	72.6	46.5
	2	7.7	20.2	73.2	46.8
	3	7.8	20.2	78.3	50.1
	4	7.8	19.1	77.7	49.7
Nwanedi river	5	7.2	20.5	696.0	445.4
	6	7.7	20.4	696.0	445.4
	7	8.0	20.3	699.0	447.4
Tshipise river	8	8.3	20.0	5270.0	3372.8
Nzhelele river	9	8.5	20.4	154.6	98.9
	10	8.5	20.5	157.5	100.8

Table 4.8: physico-chemical parameters of samples obtained in dry season

Sample site	Sample name	pH	Temperature (◦ c)	EC (mS cm^{-1})	TDS (mg L^{-1})
Mutale river	1	8.5	22.0	53.2	32.5
	2	8.5	19.5	51.8	33.8
	3	8.3	18.5	50.6	32.9
	4	7.8	18.5	51.2	32.7
Nwanedi river	5	8.1	17.0	295.0	192.7
	6	8.4	17.0	300.0	191.5
	7	8.4	17.0	298.0	190.3
Tshipise river	8	8.4	17.0	2960.4	1864.0
Nzhelele river	9	8.1	16.0	168.4	115.8
	10	8.0	16.0	169.8	106.3

4.3.2 Determination of anions

4.3.2.1 Determination of anions in river samples by using IC

Table 4.9 and 4.10 describes the average concentration of selected anions obtained from different sampling points in different seasons (dry and rainy season). The results of these studies demonstrate that the concentration of fluoride for all samples were below the instrument detectable limit (<1 mg L^{-1}) except for Tshipise river (sample 8) which had a concentration of 6.403 mg L^{-1} in rainy season and 8.419 mg L^{-1} in dry season. High concentration of fluoride could be due to different factors such as minerals or geo-chemical deposits through the process of natural weathering and leaching. The fluoride concentration from both Tshipise river samples was higher than the values set by the SANS, WHO and Canadian water guideline for drinking water. Fluoride concentration values reported from Tshipise river are similar to a value reported by Queste et al. (2001). Tshipise water may put the community in danger of fluorosis if ingested as indicated by puka (2008). However, adverse effects from domestic use are not expected as far as concentration of fluoride is concerned for Mutale, Nwanedi and Nzhelele river.

The concentration of chloride in river sample ranged from 9.282-962.495 mg L^{-1} in rainy season (Table 4.9) and 11.377-935.659 mg L^{-1} during dry season samples (Table 4.10). Nwanedi and Tshipise samples were found to contain high concentration of chloride compared to Mutale and Nzhelele river samples. The presence of high chloride concentration could be from natural occurring rocks and runoffs from agricultural fields. Nwanedi and Mutale rivers flow very close to farming areas, viz., the communities have planted fruits such as tomatoes, oranges, naartjie and vegetables close to the rivers. Moreover, farmers close to Nwanedi river use the river water for irrigation. The chloride concentrations for Mutale, Nwanedi and Nzhelele rivers were below the MAL for drinking water except for Tshipise river samples (Sample 8). Consequently, the same sample (Sample 8) contained high EC and TDS. Therefore, this is the indication of high amounts of chloride dissolved in the water. Based on these findings, Tshipise and Nwanedi river should be monitored by the relevant agencies in order to prevent environmental pollution and reduced hazards caused by activities at the sampling site. The concentrations of chloride in Nwanedi river in dry and rainy seasons were in line with the average concentration of groundwater reported by Singh et al. (2008). Phosphate was not detected which thereof suggest that phosphate occurs in the environment in trace amount.

It was observed that the concentration of nitrate ranged from 0.747-6.265 mg L^{-1} in rainy season Table 4.9. The values obtained were corresponding to average values reported by Singh et al. (2008) for dug and tube well water. The nitrate concentration in dry season ranged from <1-4.745 mg L^{-1}. However, that there was a decrease in the nitrate concentration in dry season, due to the evaporation which consistent with the dry season. Nitrate in the water body indicated that agricultural applications of manure, fertilizers and naturally occurring rocks may be a potential source of nitrate. High concentration of nitrate in the rainy season could be due to dead plants washing into the river and naturally occurring rocks containing salts. It was observed from the results of four samples (1-4) in Mutale river (Table 4.9) had varying concentrations of nitrate even though they were collected from the same river. This could be due to the fact that Mutale river is long, therefore, with different geological makeup of the area and proximity of the farming area to the sampling points contributed to the inconsistency towards the nitrate concentration. All nitrate samples were below the maximum water guideline for drinking water (Table 2.3). Higher nitrate values were obtained from Nwanedi river in both dry and rainy seasons.

It was also observed from Table 4.9 and 4.10 that the concentration of sulphate in river samples ranged from 0.523-289.657 mg L^{-1} in rainy season. Although, during dry season it ranged from 0.247-326.598 mg L^{-1}. Sample 8 from Tshipise river was reported to have the highest concentration of sulphate in both seasons which exceeds the MAL of 250 mg L^{-1} in both seasons according to WHO (2008). According to Brima (2017), high concentrations of SO_4^{2}- gives water a noticeable taste and have a laxative effect on humans.

Adverse effects are not expected from domestic use of the river (Mutale, Nwanedi and Nzhelele rivers), because their sulphate concentration were found to be below set guideline of drinking water (Table 2.3). However, the sulphate levels in the rest of the samples were below the guideline thresholds (Table 2.3). According to (Brima, 2017), high SO_4^{2-} have a laxative effect on humans and corrosive on pipe fixtures. The increase in sulphate in dry season could be due to run-off from agricultural factors such as soil erosion, domestic, farming, pesticides and fertilizers.

Table 4.9: The average concentration of anions in rainy season

		Average concentration of anions (mg L^{-1})					
Sample site	Sample name	F^-	Cl^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Mutale river	1	<1	9.282	<1	6.265	nd	1.549
	2	<1	9.649	<1	3.953	nd	1.094
	3	<1	10.850	<1	0.686	nd	0.523
	4	<1	10.775	<1	1.256	nd	0.679
Nwanedi river	5	<1	105.102	<1	4.905	nd	35.051
	6	<1	103.697	<1	5.087	nd	34.558
	7	<1	104.155	<1	5.044	nd	34.426
Tshipise river	8	6.403	962.495	<1	0.747	nd	289.657
Nzhelele river	9	<1	11.666	<1	1.163	nd	1.181
	10	<1	12.041	<1	1.724	nd	2.363

nd = not detected

Table 4.10: The average concentration of anions in dry season

Sample site	Sample name	F^-	Cl^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
Mutale river	1	<1	11.377	<1	1.727	nd	0.324
	2	<1	11.448	<1	1.730	nd	0.570
	3	<1	11.720	<1	1.718	nd	0.247
	4	<1	11.797	<1	1.724	nd	0.418
Nwanedi river	5	<1	74.095	<1	4.745	nd	26.734
	6	<1	74.334	<1	4.721	nd	26.440
	7	<1	73.810	<1	4.643	nd	26.435
Tshipise river	8	8.419	935.659	<1	<1	nd	326.598
Nzhelele river	9	<1	21.521	<1	2.489	nd	2.615
	10	<1	21.082	<1	2.406	nd	2.304

nd = not detected

4.3.2.2 Comparison of anions obtained in different season

In this work, we examined samples from different water locations (1. Mutale, 2. Nwanedi, 3. Tshipise river and 4. Nzhelele river). Figures 4.6-4.8 shows the concentration of each anion with 5% error SD for rainy and dry season.

4.3.2.2.1 Comparison of fluoride concentration

Sample 8 from Tshipse river contained high concentration of fluoride (Table 4.8 and 4.9) and exceeded the maximum permissible limit (Table 2.3). However, sample 8 also showed an increase of fluoride concentration during dry season. The reason for lower concentration of fluoride could be due to the dilution of dissolved ions in rainy season. All other samples below <1 mg L^{-1} in both dry and rainy season.

4.3.2.2.2 Comparison of chloride concentration

Figure 4.6 shows variation of the chloride concentration in rainy and dry season. It was observed that (Nwanedi and Tshipise rivers) samples 5, 6, 7 and 8 had higher concentration of chloride during rainy season, whereas samples 1, 2, 3, 4, 9 and 10 (Mutale and Nzhelele rivers) had a steady increase of the concentration of chloride in dry season. In dry season samples 1, 2, 3, 4, 9 and 10 had an increase in the concentration by a factor of 1.226, 1.186, 1.080, 1.094, 1.844 and 1.751 respectively, whereas in rainy season sample 5, 6, 7 and 8 had an increase in chloride concentration by a factor of 1.418, 1.395, 1.411 and 1.029 respectively. Higher concentrations were observed in Nzhelele river during dry season. The increase in chloride in the river samples could be from naturally occurring rocks and road salts runoff. Sample 3, 4, 5, 6 and 9 of Mutale, Nwanedi and Nzhele river were sampled at the downward location of the stream. The concentration of chloride was increasing at the downstream sites viz., sample 3 and 4. The same observation was noted with Nwanedi river samples 5 and 6 were obtained down the river and sample 9 of Nzhelele river was collected down the river as well. The distance of the farming area and the uniformity of geological makeup could have affected the difference in the concentration of chloride in the same river. The differences can be due to increase in dissolved chloride containing fertilizers and sewage input since the rivers are close to the community and farming places.

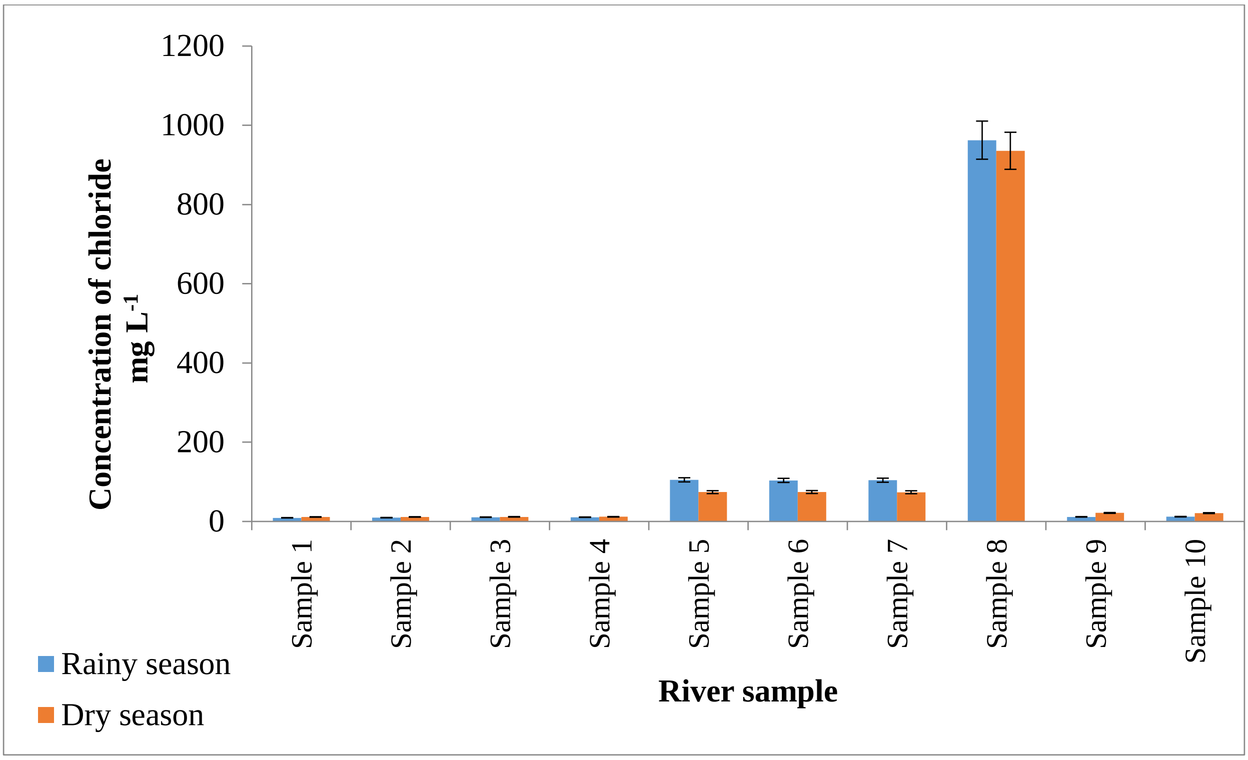

Figure 4.6: Variation of chloride concentration in dry and rainy season (% SD, n = 3)

4.3.2.2.3 Comparison of nitrate concentration

Figure 4.7 shows a variation of nitrate concentration in rainy and dry season. Samples 1, 2, 5, 6, 7 and 8 had higher concentration of nitrate during rainy season, whereas samples 3, 4, 9 and 10 were observed to have high concentration of nitrate in dry season. Sample 1, 2, 5, 6, 7 and 8 were high in concentration by a factor of 3.628, 2.285, 1.034, 1.078, 1.086 and 0.747 respectively, and samples 3, 4, 9 and 10 were higher by factor of 2.285, 1.373, 2.140 and 1.396 respectively. There was no consistency in the concentration of nitrate of Mutale river. The reason for no consistency could because of the distance between the sampling points and their proximity to the farming area. Nitrate in surface water arises from various sources, including run-off from agricultural factors such as soil erosion; domestic, farming, pesticides, sewage inputs and insecticides. The first two samples (sample 1 and 2) had high of nitrate concentration as compared to sample 3 and 4 during rainy season. Samples 1-4 (Table 4.9 and 4.10) were obtained from the same river (Mutale river) however, from different sampling points, and hence the varying in nitrate concentration. Nitrate concentration was low for sample 3 and 4.

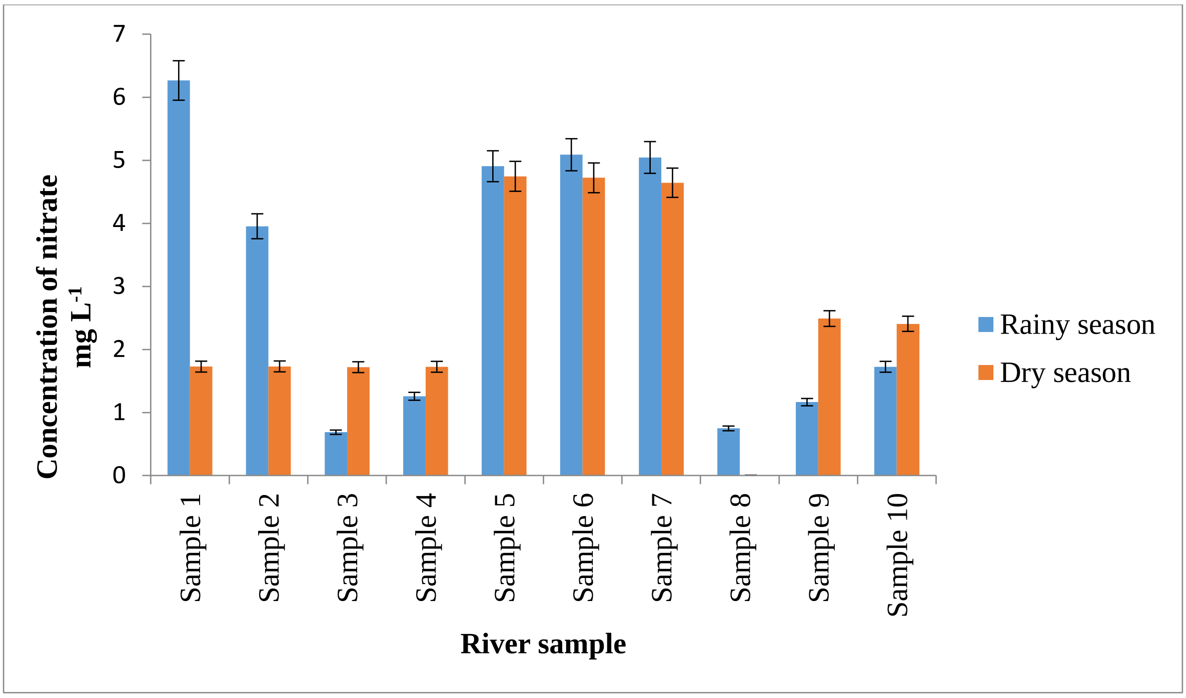

Figure 4.7: Variation of average nitrate concentration in dry and rainy season (% SD, n = 3) of Mutale, Nwanedi, Tshipise and Nzhelele river

4.3.2.2.5 Comparison of sulphate concentration

Figure 4.8 shows a variation of sulphate concentration in rainy and dry season. It was observed that samples (1, 2, 3, 4, 5, 6, 7, and 10) had higher concentration of sulphate during rainy season, whereas sample (8 and 9) had high concentration of sulphate in dry season. The differences could be due to increase in dissolved sulphate containing fertilizers, sewage input since the rivers are close to the community and farming places. The concentration of Samples 1, 2, 3, 4, 5, 6, 7 and 10 were high by a factor of 4.781, 1.919, 2.117, 1.624, 1.311, 1.307, 1.302 and 1.026 respectively, whereas (sample 8 and 9) has 1.128 and 2.214 respectively. High differences in the concentration of sulphate were observed from Tshipise river.

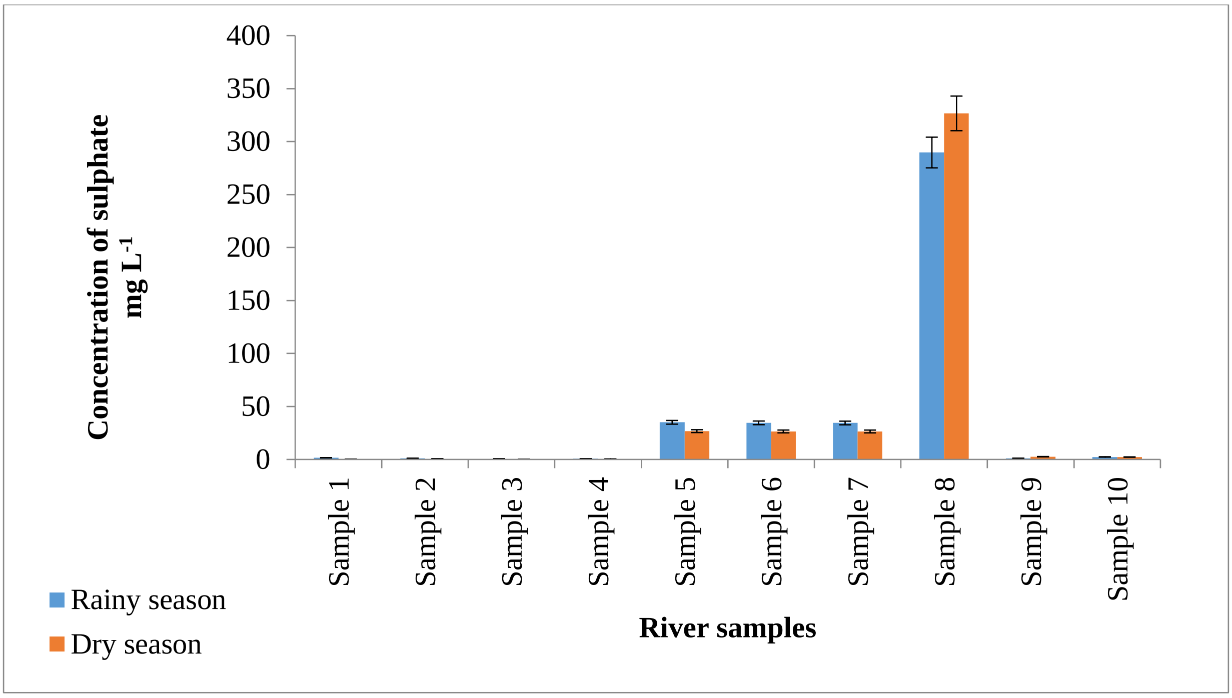

Figure 4.8: Variation of sulphate concentration in dry and rainy season (% SD, n = 3) of Mutale, Nwanedi, Tshipise and Nzhelele river

4.3.3 The determination of selected metals in water samples using ICP-OES

4.3.3.1 Determination of cations in river samples

Analysis of samples using ICP-OES were carried out for the determination of major cations concentration such as Al, Ca, Fe, K, Mg and Na. Table 4.11 shows results obtained during rainy season and Table 4.12 shows results obtained during dry season. Ions such as Ca, Mg, Na and K are part of dissolved solids in the water system Shankar and Mohan (2006) and affects the quality and taste the of water. The soil samples obtained next to the rivers also indicated the presence of Ca, Mg, Fe and Al (Table 4.6) in the area.

Mutale river

It was observed from Table 4.11, that the concentration of cations (Al, Ca, Fe, K, Mg and Na) in Mutale river samples ranged from 0.038-0.095 mg L^{-1}, 2.376-3.489 mg L^{-1}, 0.233-0.302 mg L^{-1}, 0.320-0.390 mg L^{-1}, 1.488-2.337 mg L^{-1} and 5.283-7.975 mg L^{-1} respectively in rainy season. It was also observed in dry season (Table 4.11) that the concentration of cations ranged from <DL mg L^{-1}, 0.953-2.183 mg L^{-1}, <DL-0.605 mg L^{-1}, 0.325-0.583 mg L^{-1}, 0.483-1.418 mg L^{-1} and 2.232-5.367 mg L^{-1} respectively. The concentrations of Al, Ca, F, Mg and Na were higher in rainy season, Thereof, these cations where washed and dissolved into the river. Though, Fe and K showed an increase in concentrations in dry season. In addition, the concentration of Fe in Mutale river, samples (1-4) was observed to be slightly above the MCL of 0.02 mg L^{-1}. The reason for high Fe concentration may have been caused by erosion or weathering of natural occurring rocks containing Fe. Higher concentration of Fe is an indication of levels of pollution in surface water according to Agbalagba et al. (2011). The Fe results for Mutale river corresponds with the Fe results obtained by Brima (2017) in groundwater. The concentration of all other cations, were within water regulatory standard guideline values (Table 2.3). Hence, no health implication to the public consumer are expected to occur. The increasing order of abundant concentrations in Mutale river is Al < Mg < Fe < K < Ca < Na.

Nwanedi river

Furthermore, the concentration of cations (Al, Ca, Fe, K, Mg and Na) in Nwanedi river samples (5-7), during rainy season ranged from 0.022-0.825 mg L^{-1}, 10.706-26.872 mg L^{-1}, 0.091-0.234 mg L^{-1}, 0.256-1.974 mg L^{-1}, 8.311-22.526 mg L^{-1} and 31.628-80.984 mg L^{-1}, respectively (Table 4.11). Whereas in dry season the concentrations of cations ranged from DL-0.225 mg L^{-1}, 6.695-15.799 mg L^{-1}, 0.551-0.498 mg L^{-1}, 0.135-0.717 mg L^{-1}, 6.503-15.606 mg L^{-1} and 30.798-74.117 mg L^{-1} respectively. The highest concentrations of Al, Ca, K, Mg and Na were obtained in rainy season, except Fe. The reason for low concentrations of Fe may be due to the dilutions effect of rain water. The concentration of Fe and Al of Nwanedi river samples exceeded the SANS 241 (2006) water guidelines. The distance between sampling sites in Nwanedi river had an effect on the inconsistency of the level of concentrations between the samples. The distance between the farming area to the sampling point, as well as erosion of of containing Fe and Al may be the reason for the difference in the concentration between the samples. The concentrations of the soil sample obtained in the vicinity of Nwanedi river also suggested the presence of Ca, Mg, Fe and Al (Table 4.6). This postulates, that some cations present in the water are coming from the soil. The concentrations of Ca, K, Mg and Na were within drinking water limit (Table 2.3). The increasing order of abundant concentrations in Nwanedi river is Al < Fe < K < Mg < Ca < Na.

Tshipise river

The concentration of Al, Ca, Fe, K, Mg and Na in sample 8 of the Tshipise river in rainy season were as follows 0.023 mg L^{-1}, 28.012 mg L^{-1}, 1.120 mg L^{-1}, 4.044 mg L^{-1}, 81.588 mg L^{-1} and 836.690 mg L^{-1} respectively (Table 4.11). The concentrations of cations during dry season were as follows 0.024 mg L^{-1}, 37.516 mg L^{-1}, 0.603 mg L^{-1}, 2.685 mg L^{-1}, 89.643 mg L^{-1} and 922.810 mg L^{-1} respectively. Cations such as Mg, Na and Fe in surface water arise from various sources, including run-off from agricultural factors such as soil erosion, domestic, farming, pesticides and insecticides. It was observed that the concentration of Fe, Mg and Na exceeded the drinking water limit guideline values (Table 2.3). Likewise, sample 8 also recorded higher values for Cl^-, SO_4^{2-}, TDS and EC as previously mentioned. The concentrations of K are similar to those reported by Agbalagba et al. (2011). The concentrations of Fe for this sample were similar to the Fe concentration reported by Ngah and Nwankwoala (2013). According to Nolakana (2016), excess Na causes hypertension, congenial diseases, kidney disorders and nervous disorders in human body. Higher concentration of Al, Ca, K, Mg and Na were observed during dry season, because, plants were decomposing, soil diminishing and eroding into the water bodies. The most abundant concentrations in increasing order are Al < Fe <K< Ca < Mg < Na for Tshipise river.

Nzhelele river

It was also observed that the concentrations of cations (Al, Ca, Fe, K, Mg and Na) in Nzhelele river samples during rainy season ranged from (<DL-0.170, 4.226-8.807, 0.353-0.570, 0.396-0.532, 3.269-6.980 and 6.310-13.821) mg L^{-1} respectively (Table 4.10). In dry season Table 4.11, the concentration of cations ranged from DL-0.023 mg L^{-1}, 10.429-16.343 mg L^{-1}, 0.599-0.608 mg L^{-1}, 0.328-0.447 mg L^{-1}, 8.408-14.057 mg L^{-1} and 16.468-27.872 mg L^{-1} respectively. The concentration of the following cations Al, Ca, Fe, Mg and Na were high in dry season and K was observed to be higher in rainy seasons. All cations were within drinking water guidelines (Table 2.3) except for the concentration Fe. The Fe concentrations recorded for Nzhelele river in rainy season were similar to the Fe results obtained by Akan et al. (2010). Weathering of rocks and erosion of soil containing this cations constituted to an increase in the concentration of these cations. The increasing order of abundant concentrations in Nzhelele river is Al < K < Fe < Mg < Ca < Na.

Table 4.11: Concentration of selected metals in water samples (rainy season)

		Concentration of selected metals (mg L^{-1})					
Sample site	Sample name	Al	Ca	Fe	K	Mg	Na
Mutale river	1	0.038	3.398	0.302	0.337	2.213	7.003
	2	0.047	3.353	0.299	0.342	2.313	7.487
	3	0.050	3.489	0.297	0.320	2.337	7.975
	4	0.095	2.376	0.233	0.390	1.488	5.283
Nwanedi river	5	0.825	22.999	0.223	1.715	19.819	74.899
	6	0.022	10.706	0.091	0.256	8.311	31.628
	7	0.439	26.872	0.234	1.974	22.526	80.984
Tshipise river	8	0.023	28.012	1.120	4.044	81.588	836.690
Nzhelele river	9	0.170	8.807	0.570	0.396	6.980	13.821
	10	<DL	4.226	0.353	0.532	3.269	6.310

DL = detectable limit

Table 4.12: Concentration of selected metals in water samples (dry season)

		Concentration of selected metals (mg L^{-1})					
Sample site	Sample name	Al	Ca	Fe	K	Mg	Na
Mutale river	1	<DL	1.446	0.605	0.582	0.875	3.308
	2	<DL	2.183	<DL	0.525	1.248	4.382
	3	<DL	0.953	0.553	0.583	0.483	2.232
	4	<DL	2.116	0.458	0.530	1.418	5.367
Nwanedi river	5	0.022	13.753	0.498	0.503	13.914	70.040
	6	<DL	6.695	0.551	0.135	6.503	30.798
	7	0.025	15.799	0.462	0.717	15.606	74.117
Tshipise river	8	0.024	37.516	0.603	2.685	89.643	922.810
Nzhelele river	9	<DL	16.343	0.599	0.328	14.057	27.872
	10	0.023	10.429	0.608	0.447	8.408	16.468

DL= detectable limit

4.3.3.2 Water hardness

Most minerals are dissolved in the aquatic system (Organization, 2008). The presence of ion is influenced by factors such as chemical weathering of rocks and dissolved minerals (Pradhan and Pirasteh, 2011). According to Shankar and Mohan (2006) ions such as Ca^{2+}, Mg^{+}, Cl^{-} and SO_4^{2-} cause water hardness, therefore, water becomes unsuitable for consumption. Hardness may cause health problems to humans, such as kidney failure (Vasanthavigar, 2012). Water containing calcium carbonate at concentrations below 60 mg L^{-1} is said to be slightly hard, whereas 60-120 mg L^{-1} is moderately hard, 120-180 mg L^{-1} is hard and more than 180 mg L^{-1} is said to be very hard (McGowan, 2000; Abegaz, 2005). Hardness can be discussed in terms of carbonate and non-carbonate hardness (Organization, 2010). Calcium is an important constituent of a number of minerals. The excess presence of calcium and magnesium in water samples causes water to be hard (Cheepi, 2012; Kožíšek, 2003; Abegaz, 2005). Water with a hardness of less than about 100 mg L^{-1} have a low buffering capacity and may be more corrosive to water pipes (Organization, 2010). Water hardness of this study was determined from the concentration of calcium and magnesium, which is defined as carbonate hardness. Total hardness is defined as TH= (2.497 Ca + 4.11 Mg); where Ca and Mg are expressed in mg L^{-1} (Pradhan and Pirasteh, 2011).

The total hardness for the rivers is displayed in Table 4.13. In rainy season, the total hardness of water for Mutale, Nwanedi, Tshipise and Nzhelele rivers ranged from 12.1-18.3 mg L^{-1}, 61.0.5-159.9 mg L^{-1}, 405.9 mg L^{-1} and 24.0-50.7 mg L^{-1} respectively, whereas, in dry season the total hardness of water was observed to range from 4.4-11.1 mg L^{-1}, 43.5-103.7 mg L^{-1}, 462.8 mg L^{-1} and 60.7-98.7 mg L^{-1} respectively. Samples collected in rainy season showed higher concentrations of hard water as comparing to dry season. It was observed that Mutale and Nzhelele river samples contained slightly hard water (Table 4.13). However, Nzhelele river samples contained moderately hard water in dry season. The reason why Mutale and Nzhelele rivers samples contain slightly hard water is because the concentration of Ca and Mg in water were very low in both the seasons (Table 4.11 and 4.12). Therefore, Mutale river **(**Samples 1-4) and Nzhelele river (samples 9-10) are not expected to cause any problem if water is utilised for irrigation. Due to elevated concentration of calcium and magnesium in rainy season, Nwanedi and Tshipise rivers contained samples (5, 7 and 8) with hard water and very hard water respectively. Furthermore, in dry season Nwanedi river samples (5 and 7) changed to moderately hard water. However, one sample from Nwanedi river (sample 6) contained moderately hard water during rainy season and slightly hard water during dry season, due to the decrease on the concentration of Ca and Mg in dry season.

Table 4.13: Water quality based on water hardness on river samples

Classification of total hardness of water (TH) as $CaCO_3$ (mg L^{-1})

River sites	Sample name	TH in rainy season	Water hardness class	TH in dry season	Water hardness class
Mutale r	1	17.6	Slightly hard water	7.2	Slightly hard water
	2	17.9	Slightly hard water	10.6	Slightly hard water
	3	18.3	Slightly hard water	4.4	Slightly hard water
	4	12.1	Slightly hard water	11.1	Slightly hard water
Nwanedi	5	139.0	Hard water	91.6	Moderately hard water
	6	61.0	Moderately hard water	43.5	Slightly hard water
Tshipise	7	159.9	Hard water	103.7	Moderately hard water
	8	405.9	Very hard water	462.8	Very hard water
Nzhelele	9	50.7	Slightly hard water	98.7	Moderately hard water
	10	24.0	Slightly hard water	60.7	Moderately hard water

4.3.3.3 Sodium hazardous classification

The concentration of sodium is important for determining the quality of water used for irrigation. Sodium hazard in irrigation water is expressed by determining the sodium adsorption ratio (SAR) and is expressed in meq L^{-1}. The SAR is given by the equation below:

$$\mathbf{SAR} = \frac{Na}{\sqrt{\frac{Ca+Mg}{2}}}$$

EC and sodium concentration are very important in classifying the quality of irrigation water. It has been observed that salts in irrigation water are affecting the growth of the plants (Singh et al., 2008). Sodium is usually associated with chloride, thus, sodium may be coming from the same source as chloride in the water. Excessive sodium content in water makes it unsuitable for irrigation purpose (Canada, 2017). It was reported that irrigating with poor quality water reduces soil productivity, changes soil physical and chemical properties and ultimately reduces yield (Sarkar and Hassan, 2006). Table 4.14 shows the classification of sodium hazard in water (Bauder, 2011).

Table 4.14: General classification of sodium hazard in water based on SAR values

SAR values meq L^{-1}	Sodium hazard of water	Comments
1-9	Low	Use on sodium sensitive crops must be cautioned
10-17	Medium	Amendment (such gypsum) and leaching needed
18-25	High	Unsuitable for continuous use
25	Very high	Unsuitable for us

It was observed from Table 4.15 that Mutale and Nzhelele rivers contained water with SAR of <18 meq L^{-1}, therefore, these rivers contain water that can be good for irrigation. Low sodium content in dry and rainy season caused water to have low SAR. It was also observed Nwanedi river samples (sample 5-7) had low SAR in rainy season, however, in dry season sample 5 and 7 contained water with high SAR. Consequently sample 5 and 7 are not suitable for prolong use. Tshipise river in dry and rainy season contained very high SAR (113.02-115.73 meq L^{-1}) than the recommended limit. Thus, suggest that Tshipise river water is unsuitable for irrigation. Increasing SAR was observed from samples 4-10 in dry season.

Table 4.15: Water quality based on sodium hazardous in river samples

Classification of Sodium hazardous classification (meq L^{-1})

River sites	Sample name	SAR dry season	Water class	SAR rainy season	Water class
Mutale	1	4.18	Low	3.07	Low
	2	4.45	Low	3.35	Low
	3	4.67	Low	2.63	Low
	4	3.80	Low	4.04	Low
Nwanedi	5	16.19	Low	18.83	High
	6	10.26	Low	11.99	Low
Tshipise	7	16.30	Low	18.70	High
	8	113.02	Very high	115.73	Very high
Nzhelele	9	4.92	Low	7.15	Low
	10	3.26	Low	5.366	Low

The Na^+ in irrigation water is usually denoted as Na^+ % (Ramesh and Elango, 2012) and can be determined by using the formula given below:

$$\textbf{Na \%} = \frac{(Ca^{+}+K^{+})}{Ca^{2+}+Mg^{2+}+K^{+}}$$

Vasanthavigar et al. (2012), described the Na % class of water as shown in Table 6.8. If Na % is > 60 then it is considered (undoubtful) meaning the water is unsuitable for irrigation and if < 60 then it is considered permissible.

Table 4.16 describe the Na % in river samples for both rainy and dry season. It was observed in rainy season that Tshipise river samples (1, 2, 3 and 4) contained water with permissible Na %. However, in rainy season samples 1 and 4 contained undoubful Na %, this is due to the increment of the concentration of Na during dry season. Nwanedi river samples 5-7 contained water with high Na % in both rainy and dry seasons (Table 4.16), which means the river water is undoubful to use for irrigation purposes. Tshipise river sample 8 also contained water with high Na % in both seasons, therefore it is undoubful to use for irrigation. Nzhelele river samples

9-10 were observed to have > 60 (Na %) in both dry and rainy season, which thereof, the river water class is permissible to use for irrigation with no harm.

Table 4.16: Classification of river water samples in Na % for rainy season

Classification of Na % (Vasanthavigar et al., 2012)					
River sites	Sample name	Na % dry season	Water class	Na % rainy season	Water class
Mutale	1	56.68	Permissible	62.63	Doubtful
	2	58.01	Permissible	58.85	Permissible
	3	58.74	Permissible	66.22	Doubtful
	4	59.48	Permissible	62.53	Doubtful
Nwanedi	5	64.15	Doubtful	71.83	Doubtful
	6	62.64	Doubtful	70.09	Doubtful
Tshipise	7	62.68	Doubtful	70.44	Doubtful
	8	88.47	Unsuitable	87.92	Unsuitable
Nzhelele	9	47.38	Permissible	48.12	Permissible
	10	47.72	Permissible	47.31	Permissible

4.3.4 Comparison of cations in different season

Figures 4.9-4.18 show variation of cation concentrations in rainy and dry season for samples 1-10. All samples contained Al, Ca, Fe, K, Mg and Na in both seasons. Sample 1 (Figure 4.9) had higher concentrations of Al, Ca, Mg and Na during rainy season, whereas Fe and K were observed to be high during dry season. According to Dinka et al. (2016) leaching of soil erosion from rocks such as limestone, dolomite, calcite and magnesite pollution from sewage and industrial waste can also contribute to high concentration of Ca and Mg. It was observed from Figure 4.10 that the concentrations of Al, Ca, Mg, Fe and Na were high in rainy season, whereas K was high in dry season. Although sample 1 and 2 are both from Mutale river, there were differences when it comes to the increase of Fe during rainy season as shown in sample 2.

Figure 4.11 showed higher concentrations of Al, Ca, Mg and Na during rainy season, whereas Fe and K were high in dry season. Sample 3 showed similar trend of the concentration of cation as in sample 1. Figure 4.12 had higher concentrations of Al, Ca and Mg during rainy season. The increase in concentration of Fe, K and Na were observed in dry season. Similar observations were observed from samples 1, 3 and 4 of Mutale river.

Figure 4.13 had higher concentrations of Al, Ca, Mg, K and Na in rainy season with an increase of Fe in the dry season. It was observed when comparing the two seasons, that Figure 4.14 showed high concentrations of Al, Ca and Na in rainy season, but Fe, K and Mg were high in dry season. Whereas Figure 4.15 showed increasing trend of Al, Ca, Mg, K and Na in rainy season and Fe was high in dry season. It was observed from Figure 4.16 had higher concentration of Fe and K in rainy season, whereas, Al, Ca, Mg and Na were observed to be high in dry season. Sample 9 from Nzhelele river (Figure 6.17) had high concentration of Al and K in rainy season, whereas high concentration of Al, Ca, Mg, Fe and Na in dry season. Sample 10 had higher concentration of K in rainy season (Figure 6.18), whereas high concentrations of Al, Ca, Mg, Fe and Na were observed in dry season. Mutale and Nzhelele river have a positive correlation, they both were showing increasing trends (Al, Ca, Mg, TH, SAR and Na %) in rainy season and Nwanedi and Tshipise rivers were showing similar trends (Ca, Fe, Al, TH, SAR and Na%) in dry season.

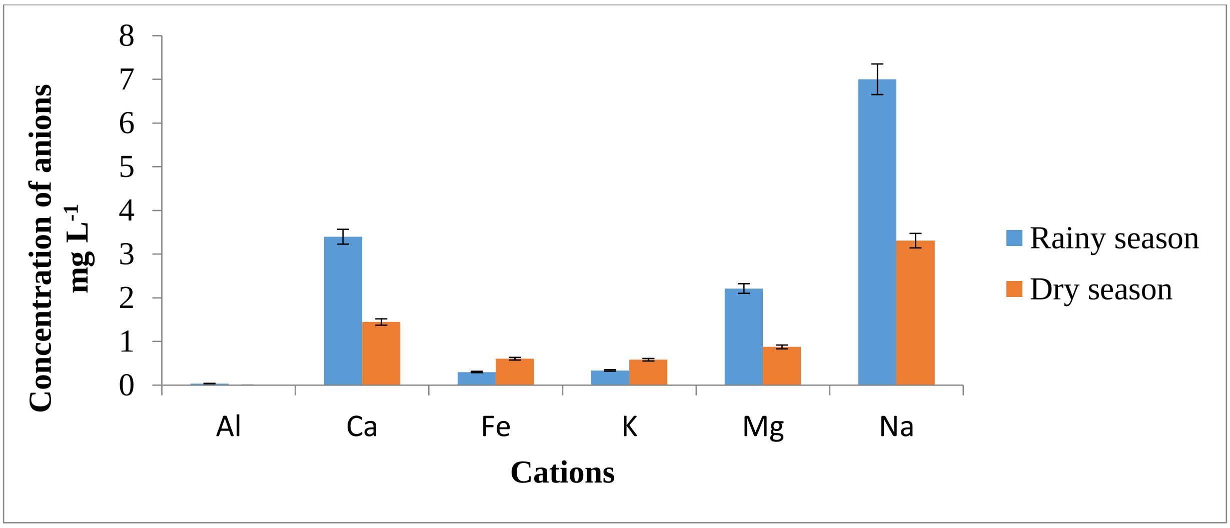

Figure 4.9: Variation of cations concentration in dry and rainy season (% SD, n = 3) in sample 1 of Mutale river

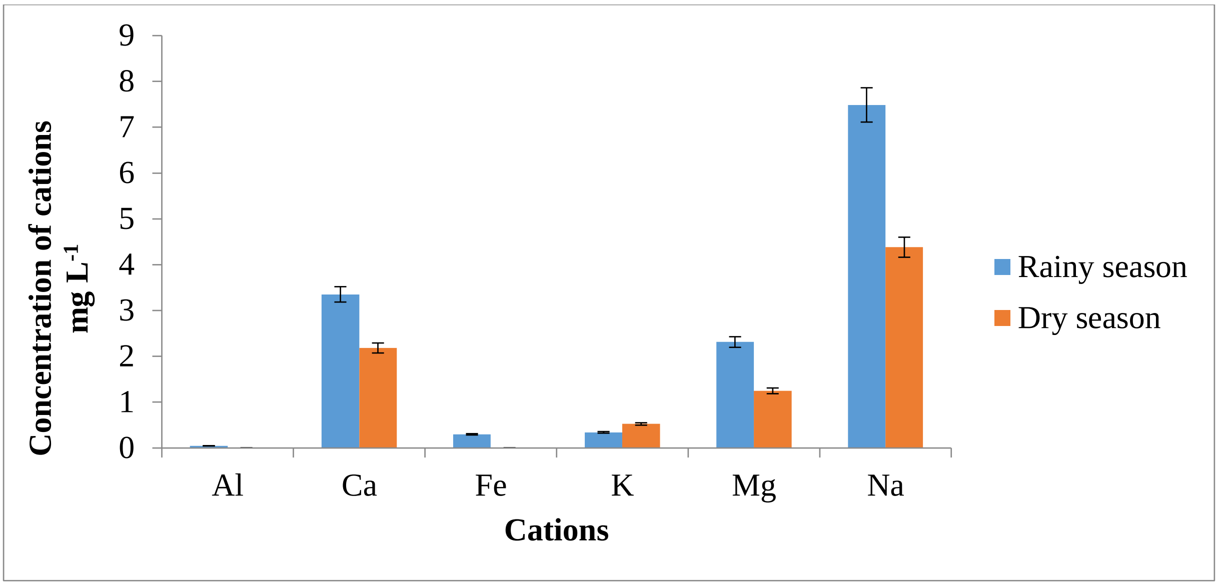

Figure 4.10: Variation of cations concentration in dry and rainy season (% SD, n = 3) in sample 2 of Mutale river

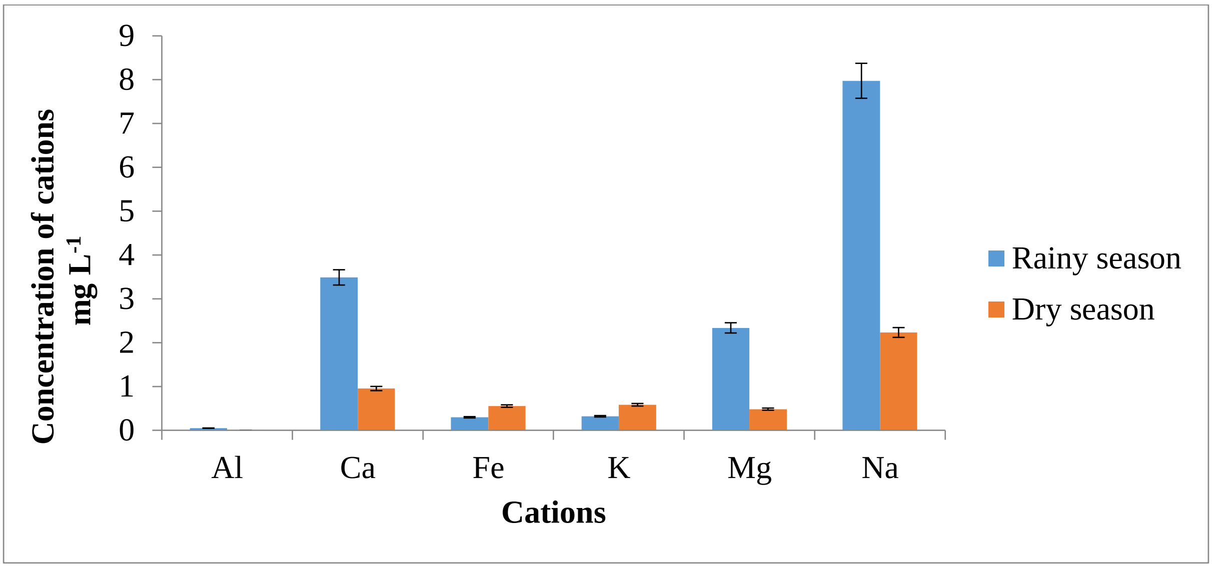

Figure 4.11: Variation of cations concentration in dry and rainy season (% SD, n = 3) in sample 3 of Mutale river

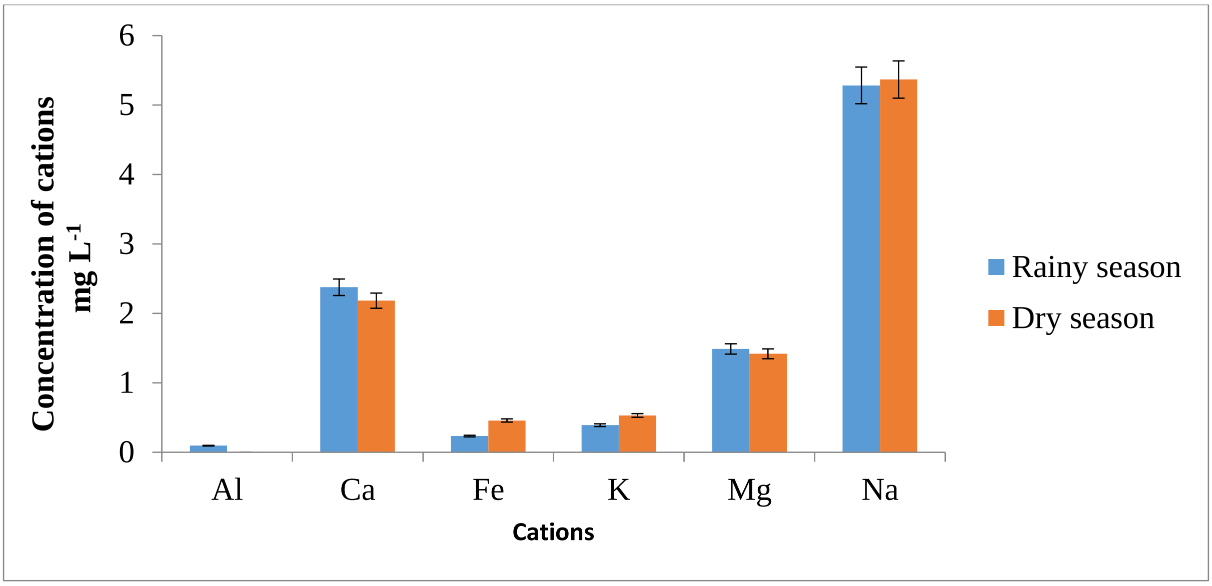

Figure 4.12: Variation of cations concentration in dry and rainy season (% SD, n = 3) in sample 4 of Mutale river

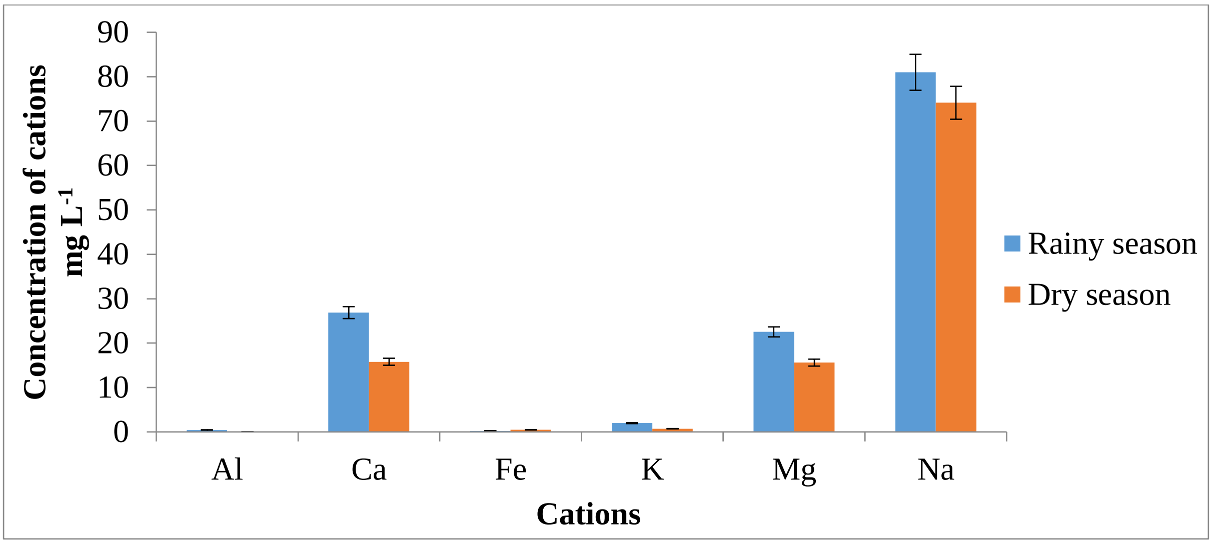

Figure 4.13: Variation of cations concentration in dry and rainy season (% SD, n = 3) in sample 5 of Nwanedi river

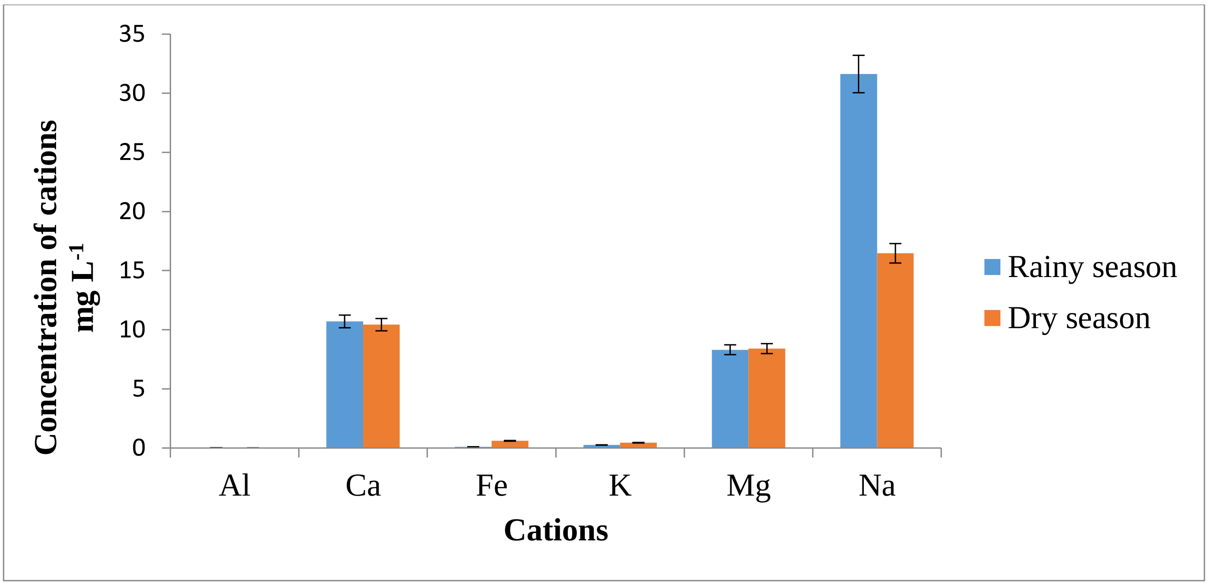

Figure 4.14: Variation of cations concentration in dry and rainy season (% SD, n = 3) in sample 6 of Nwanedi river

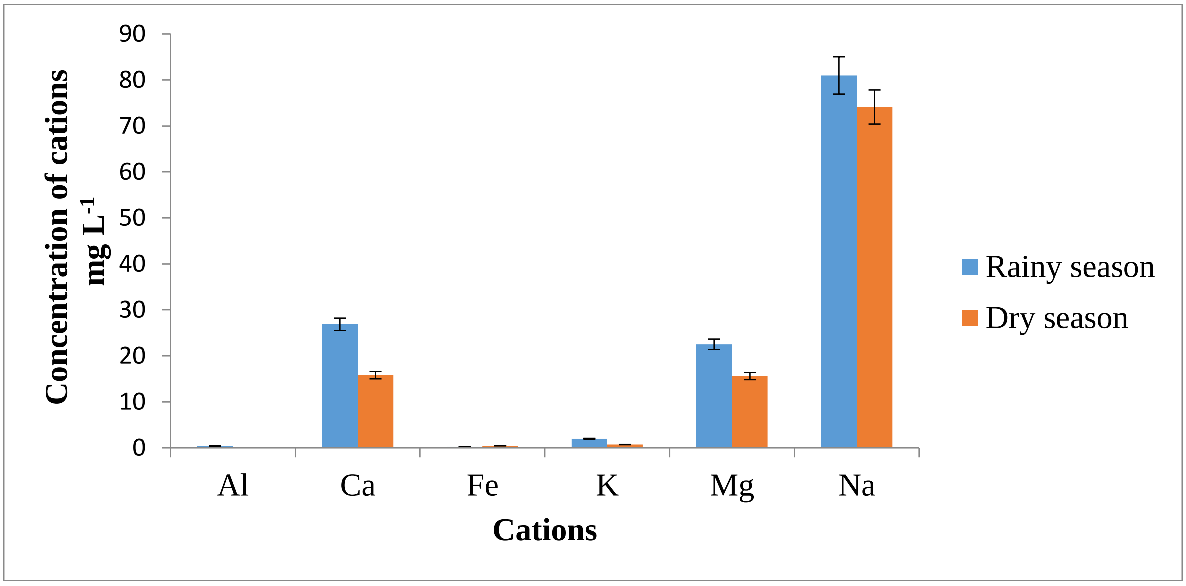

Figure 4.15: Variation of cations concentration in dry and rainy season (% SD, n = 3) in sample 7 of Nwanedi river

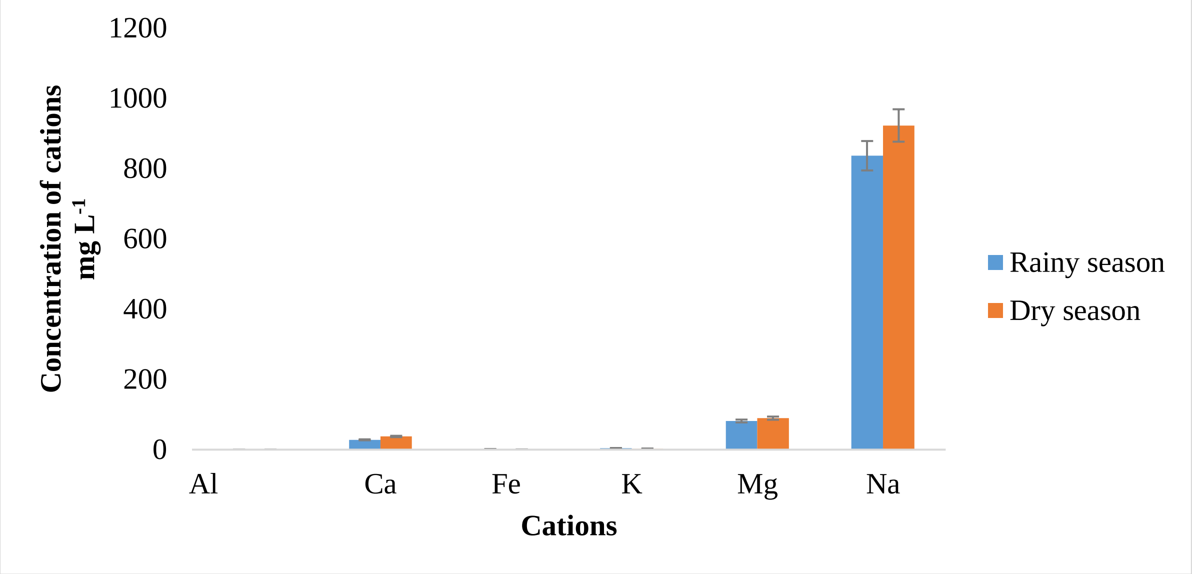

Figure 4.16: Variation of cations concentration in dry and rainy season (% SD, n = 3) in sample 8 of Tshipise river

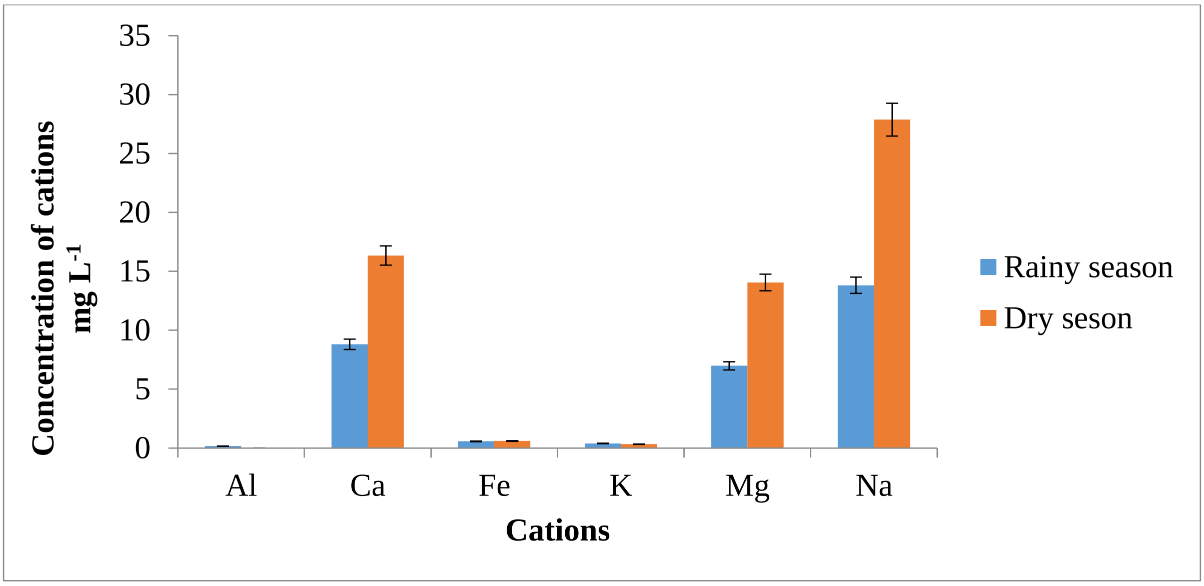

Figure 4.17: Variation of cations concentration in dry and rainy season (% SD, n = 3) in sample 9 of Nzhelele river

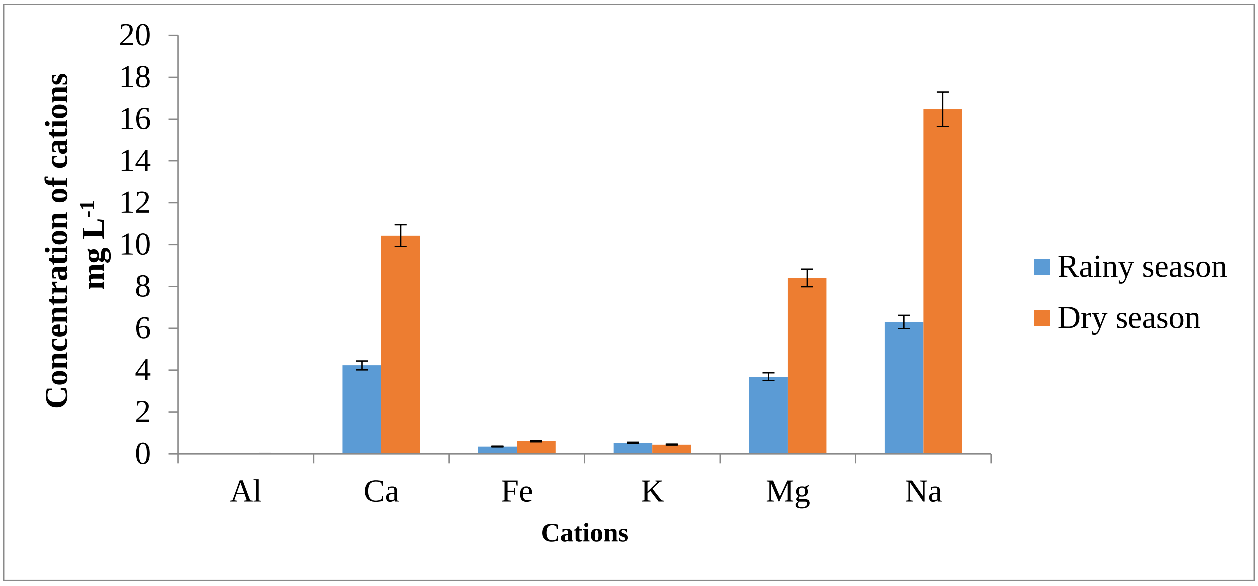

Figure 4.18: Variation of cations concentration in dry and rainy season (% SD, n = 3) in sample 10 of Nzhelele river.

4.3.5 Determination of trace metals in river samples by ICP-MS

The results indicated the presence of the following trace metals (Li, V, Cr, Co, Ni, Cu, Zn, As, Mo, Cd, Tl and Pb) during both sampling seasons as shown in Table 4.16 and 4.17. The soil sample obtained close to the rivers also suggested the presence of V, Cr, Co, Ni, Cu, Zn, As and Tl (Table 4.6).

Mutale river

It was observed from Table 4.17 that the concentrations of trace metals (Li, V, Cr, Co, Ni, Cu, Zn, As and Mo) in rainy season were slightly higher concentrations than in dry season. The reason for higher concentrations in rainy season was because trace metals were washed from soils and accumulate into the river. The highest concentration of Zn was obtained from Mutale river with concentration of 3.703-13.362 µg L^{-1} in rainy season and 3.794-25.205 µg L^{-1} in dry season, whilst the lowest concentrations were Cd (DL µg L^{-1}) and Tl (DL µg L^{-1}). This is due to the fact that Cd and Tl occur in low concentrations in the environment. The source of zinc could be from naturally occurring and soil leaching from soil. According to He et al. (2005), trace elements in an agro-ecosystem are either coming from soil parent materials or anthropogenic inputs. In addition, the occurrence of these metals at high concentrations may be detrimental to the environment. (Awofolu et al., 2005). All Mutale samples contained low concentration of trace metals and were within the guideline values from all organisation (Table 2.3).

Nwanedi river

Li, V, Cr, Co, Ni, Cu, Zn, As and Mo ranged from (0.074-0.811, 1.811-7.946, <DL-3.185, <DL-0.422, 0.693-6.93, 0.299-1.659, 0.714-11.736, 0.098-0.925 and 0.230-0.830) µg L^{-1}, respectively, in rainy and dry season (Table 4.17 and 4.18). It was observed that the concentration of all trace metals were within the standard limit for drinking water as per guideline (Table 2.3). The concentrations of Li, V, Cr, Co, Ni, Cu and Zn were slightly higher in rainy season, whilst As and Mo were slightly higher in dry season. Probable reason for high concentrations in rainy season may have been caused by erosion or weathering of naturally occurring rocks that contains metals and surface runoffs from agricultural land. Sample 6 in Nwanedi river had the least concentration of trace metals among other samples (sample 5 and 7). Because sampling point of sample 6 was situated (in the upper stream) further apart from sample 5 and 7, hence, these suggest that the concentration of metals increases as the river flows down the stream. The concentration of Cd and Tl were found to be below the detectable limit for all samples in both rainy and dry season.

Tshipise river

It was also observed in Table 4.17 and 4.18 from Tshipise river sample that the concentration of trace metals (Li, V, Cr, Ni, Cu, Zn, As and Mo) were as follows (2.348-2.762, 9.561-15.952, 0.091-0.196, 0.693-0.693, 1.579-1.587, 2.250-2.344, 8.965-10.017 and 10.017-11.267) µg L^{-1} respectively in rainy and dry season. The concentration for all trace metals were less than the standard limit for drinking water (Table 2.3), except for As which has exceeded the MCL for drinking water (10 µg L^{-1}). The reason for high concentration may have been caused by the application of pesticides, erosion and weathering of soil (Singare et al., 2012). The soil sample next to Tshipise river also suggested the presence of high As concentration (Table 4.6), therefore, some of the metals were leached from the soil. The concentration of Co, Cd and Tl were found to be below the detectable limit hence these elements are not expected to cause any problem if the water is utilised for irrigation. The highest concentration of trace metal in the river sample was V and conversely the least concentrations were Cd and Tl. All determined concentrations were observed to be high during rainy season, than dry season, except for As and Mo. Molybdenum is found naturally in soil (WHO, 2008). Thus available in abundant in water. The reason for high available concentration during rainy season could have been because of the rain, most metals were dissolved into the rivers from soil and fertilisers from nearby farming places. The concentration of Ni for samples 5 and 7 were similar to the concentration values reported by Akan et al. (2010). Nickel is known to be immunotoxic, dermatitis or asthma (Singare et al., 2012).

Nzhelele river

It was detected that the concentration levels of trace metals (Li, Cr, Co, Ni, Cu, Zn, As and Mo) in Nzhelele river ranged from (0.052-0.158, <DL-0.211, <DL-0.369, 0.918-4.758, 0.392-0.966, 1.218-12.444, 0.072-0.386 and 0.206-0.448) µg L^{-1}, respectively (Table 4.17 and 4.18). Nzhelele river samples were observed to have low concentration of V, Cr, Co, Cd, Tl and Pb and high concentration of Zn. High concentration of Zn was also observed in Nzhelele soil sample results (Table 4.6), which means Zn is attributed to leaching from the soil sample. According to Canadian guideline (2017), high concentration can be caused by anthropogenic sources such as natural sewage and domestic waste. Trace metals such as Cd, Tl and Pb occurs in the environment at low concentrations. The concentration of all trace metals were within drinking water guidelines (Table 2.3). The concentration of all determined trace metals were observed to be high in rainy season as compared to dry season, exept for As and Mo). The reason for high available concentration during the rainy season is due to rain facilitating in weathering, and soil erosion. The concentration of Co in rainy season for sample 9 and 10 was corresponding with reported Co values obtained by Brima (2017).

Table 4.17: Concentration of selected trace metals in rainy season

	Concentration ($\mu g\ L^{-1}$)									
Metals	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Li	0.118	0.022	0.165	0.150	0.811	0.657	0.657	2.762	0.158	0.052
V	0.553	0.216	0.359	0.486	7.940	1.811	7.946	15.795	<DL	<DL
Cr	0.927	0.138	0.704	1.871	3.185	<DL	1.271	0.196	0.211	<DL
Co	<DL	<DL	0.029	<DL	0.422	<DL	0.335	<DL	0.229	0.369
Ni	2.542	2.467	1.970	0.679	1.474	1.022	5.240	1.556	4.758	1.947
Cu	1.751	1.612	2.810	2.691	1.659	0.733	1.251	1.587	0.966	0.409
Zn	11.955	3.794	17.425	25.205	11.736	0.877	9.658	2.344	12.444	9.214
As	0.105	0.077	0.088	<DL	0.709	0.475	0.925	8.965	0.072	0.330
Mo	0.307	0.24	0.201	0.236	0.475	0.665	0.303	11.267	0.206	0.316
Cd	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Tl	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Pb	0.107	0.116	<DL	0.414	0.364	<DL	0.425	<DL	<DL	<DL

Mutale river =(S1-S4) Nwanedi river= (S5-S7) Thipise river = S8 Nzhelele river = (S9-S10) DL = detection limit4

Table 4.18: Concentration of selected trace metals in dry season

	Concentration (µg L^{-1})									
Metals	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Li	<DL	<DL	<DL	0.140	0.227	0.074	0.321	2.348	0.113	0.072
V	<DL	<DL	<DL	<DL	4.510	3.694	7.195	9.561	<DL	<DL
Cr	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.091	<DL	<DL
Co	<DL	<DL	<DL	<DL	0.422	<DL	0.335	<DL	0.229	0.369
Ni	0.788	1.018	0.385	0.506	0.693	0.543	0.761	0.693	1.336	0.918
Cu	<DL	0.377	0.789	0.624	0.639	0.299	0.872	1.579	0.872	0.392
Zn	3.703	3.310	6.768	13.362	0.956	0.714	1.887	2.250	2.250	1.218
As	<DL	0.014	0.003	0.098	0.896	0.541	1.255	10.017	0.355	0.386
Mo	0.163	0.167	0.173	0.230	0.830	0.566	1.006	14.066	0.448	0.289
Cd	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Tl	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Pb	<DL	<DL	<DL	<DL	<DL	<DL	0.425	<DL	<DL	<DL

Mutale river =(S1-S4) Nwanedi river= (S5-S7) Thipise river = S8 Nzhelele river = (S9-S10) DL = detection limit

4.3.6 Comparison of trace metals in different season

Figures 4.18-4.28 shows a variation of cation concentrations in both rainy and dry seasons for Samples (1-10). Figure 4.19 had higher concentration of Li, V, Cr, Ni, Cu, Zn, As, Mo and Pb during rainy season, whereas in dry season the concentration of Co was observed to be high. Figure 4.20 had higher concentration of Li, V, Cr, Ni, Cu, Zn in rainy season the concentration of As and Mo were high in dry season. Figure 4.21 had high concentration of trace metals Li, V, Cr, Co, Ni, Cu, Zn and As in rainy season and the concentration of Mo was observed in dry season. Figure 4.22 showed higher concentration of Li, V, Cr, Ni, Cu, Zn, Mo and Pb in rainy season and higher concentration As was observed in dry season. Higher concentrations of Li, V, Cr, Co, Cd, Ni, Cu and Zn in Figure 4.23 were observed in rainy season, whereas, in dry season an increase of As and Mo were observed. Figure 4.24 showed higher concentration of Li, Ni, Cu, Zn and Mo in rainy season, whereas in dry season V and As were observed to be high. Figure 4.25 had higher concentration of Li, V, Cr, Co, Ni, Cu, Zn and Pb in rainy season and the concentration of As and Mo were higher in dry season. Figure 4.26 had higher concentrations of Li, V, Cr, Co, Cd, Ni, Cu and Zn during rainy season, the increase of concentration Co, As and Mo were observed dry season. Figure 4.27 showed an increase in concentration of Li, Ni, Cu, Zn and As in rainy season, whereas a notable increase in the concentration of Mo was observed in dry season. Figure 4.28 had higher concentrations of Li, V, Cr, Co, Cd, Ni, Cu and Zn in rainy season, As and Mo was high in the dry season. Edekpyayi et al. (2016) indicated that high concentrations of metals in wet seasons comes from surface runoffs (from various land use activities in the catchment, such as settlements, dumpsites, agriculture) and dilution due to high precipitation whereas in the dry season, the major factor is evaporation from water bodies, which can lead to an increase in the concentrations.

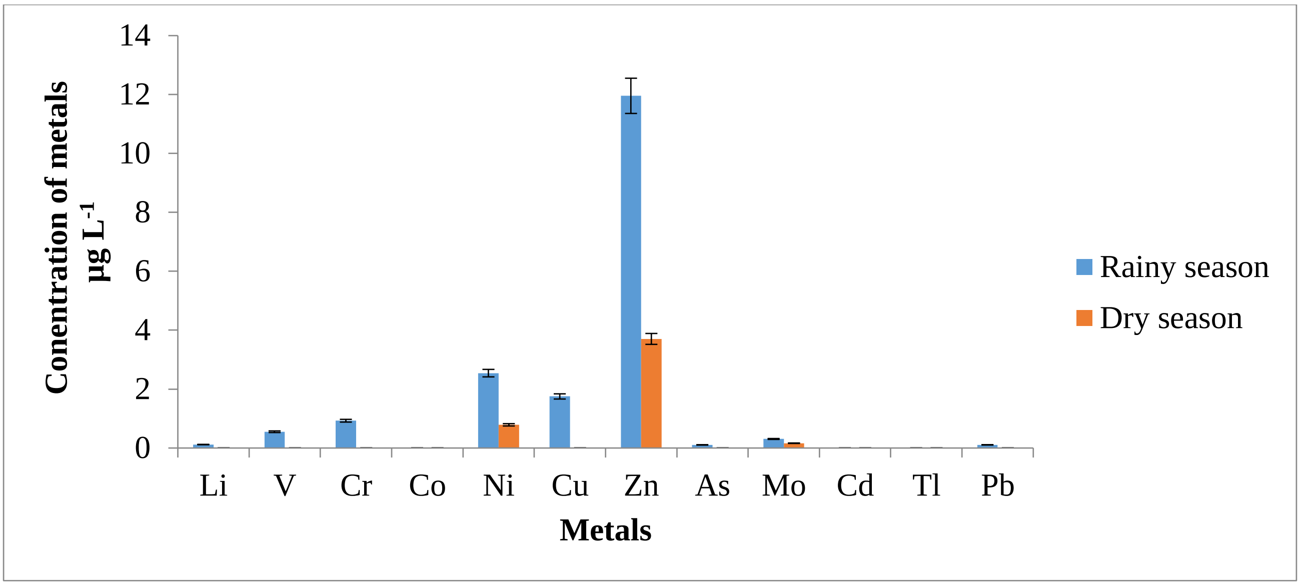

Figure 4.19: Variation of trace metals concentration in dry and rainy season (% SD, n = 3) in sample 1 of Mutale river

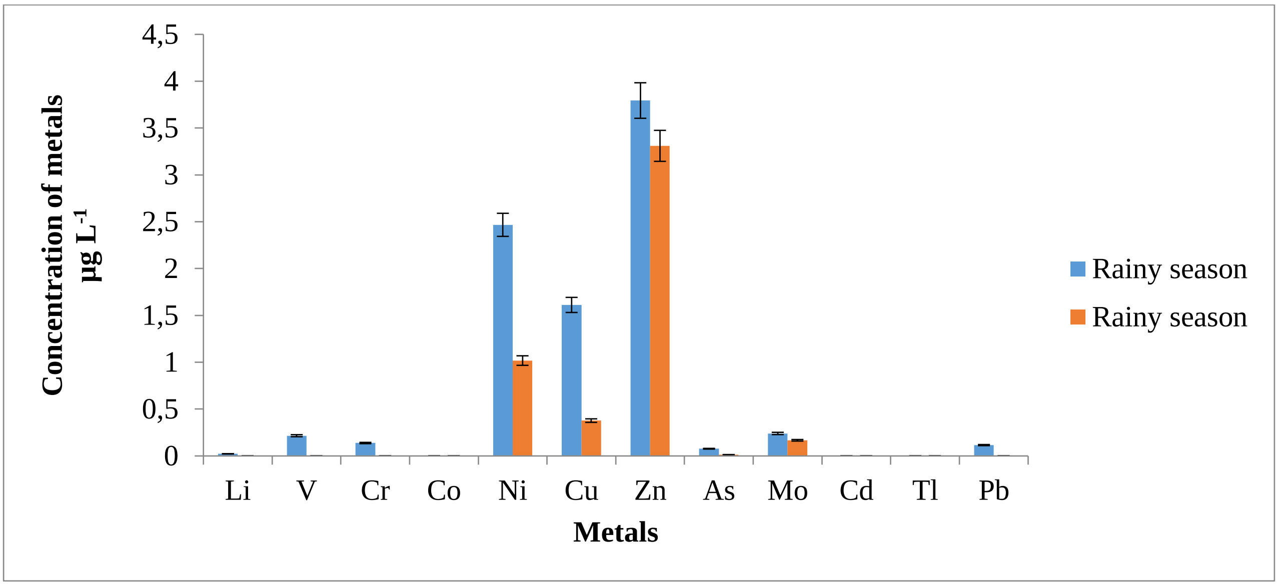

Figure 4.20: Variation of trace metals concentration in dry and rainy season (% SD, n = 3) in sample 2 of Mutale river

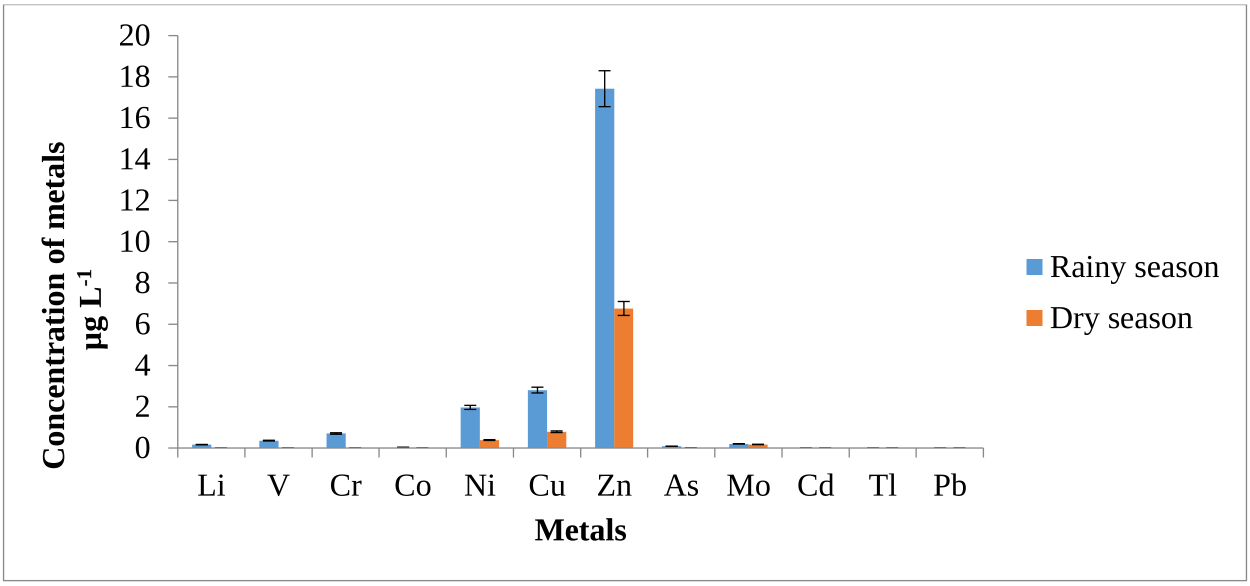

Figure 4.21: Variation of trace metals concentration in dry and rainy season (% SD, n = 3) in sample 3 of Mutale river

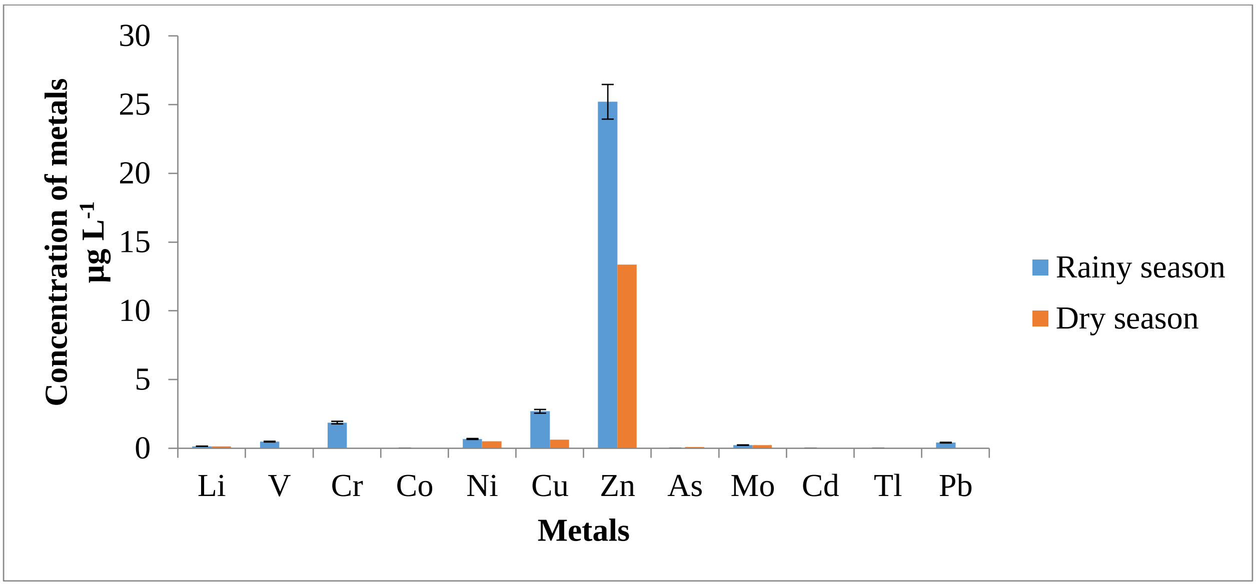

Figure 4.22: Variation of trace metals concentration in dry and rainy season (% SD, n = 3) in sample 4 of Mutale river

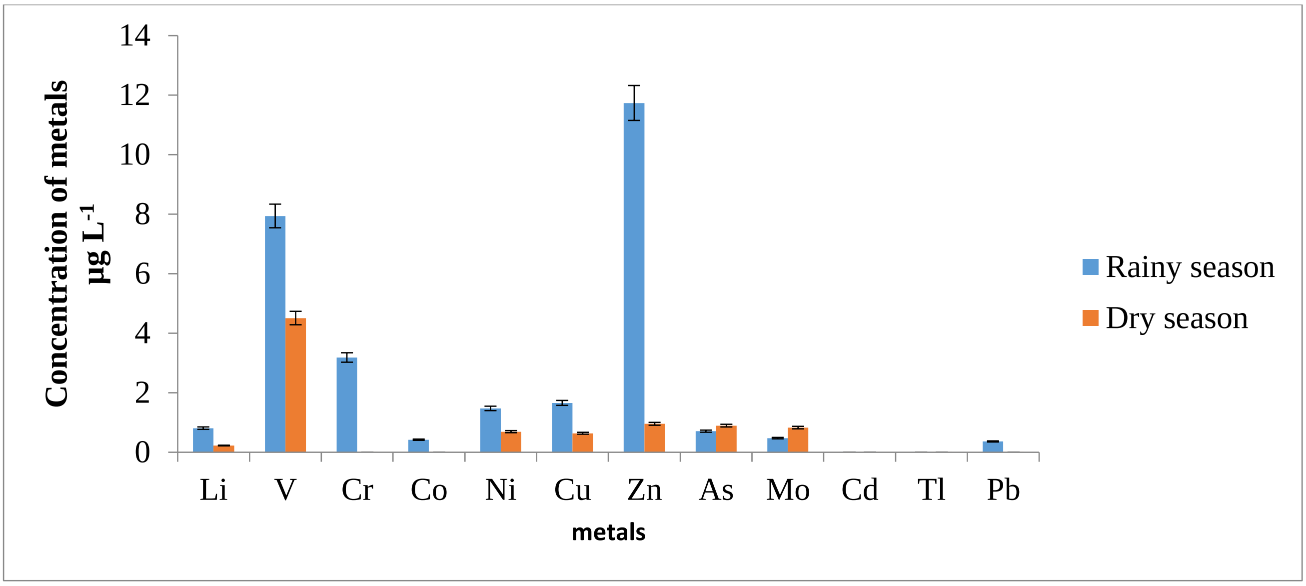

Figure 4.23: Variation of trace metals concentration in dry and rainy season (% SD, n=3) in sample 5 of Nwanedi river

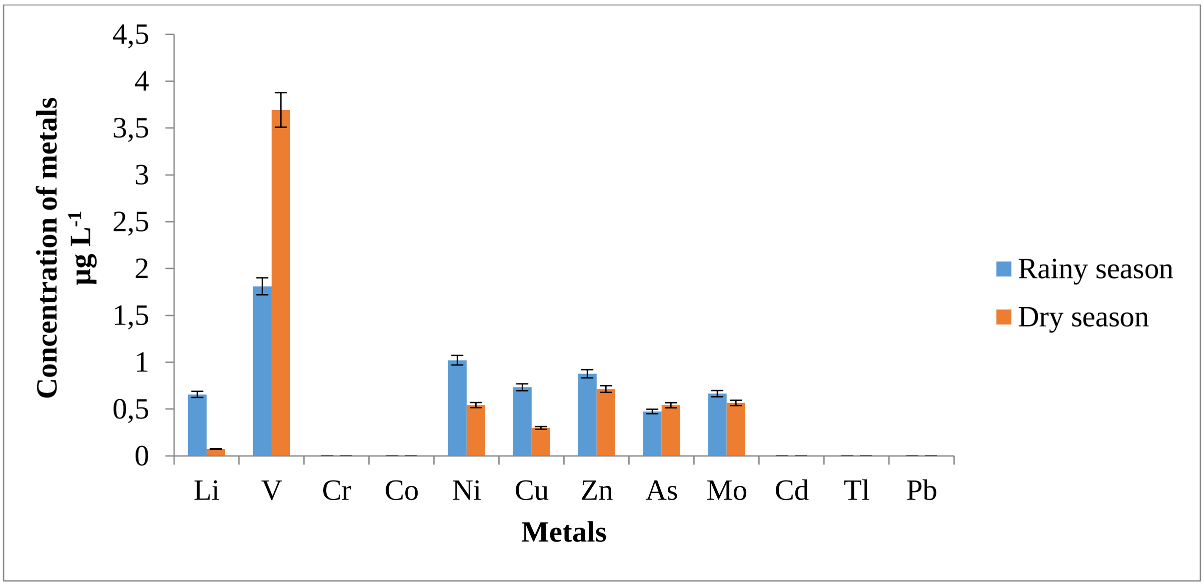

Figure 4.24: Variation of trace metals concentration in dry and rainy season (% SD, n = 3) in sample 6 of Nwanedi river

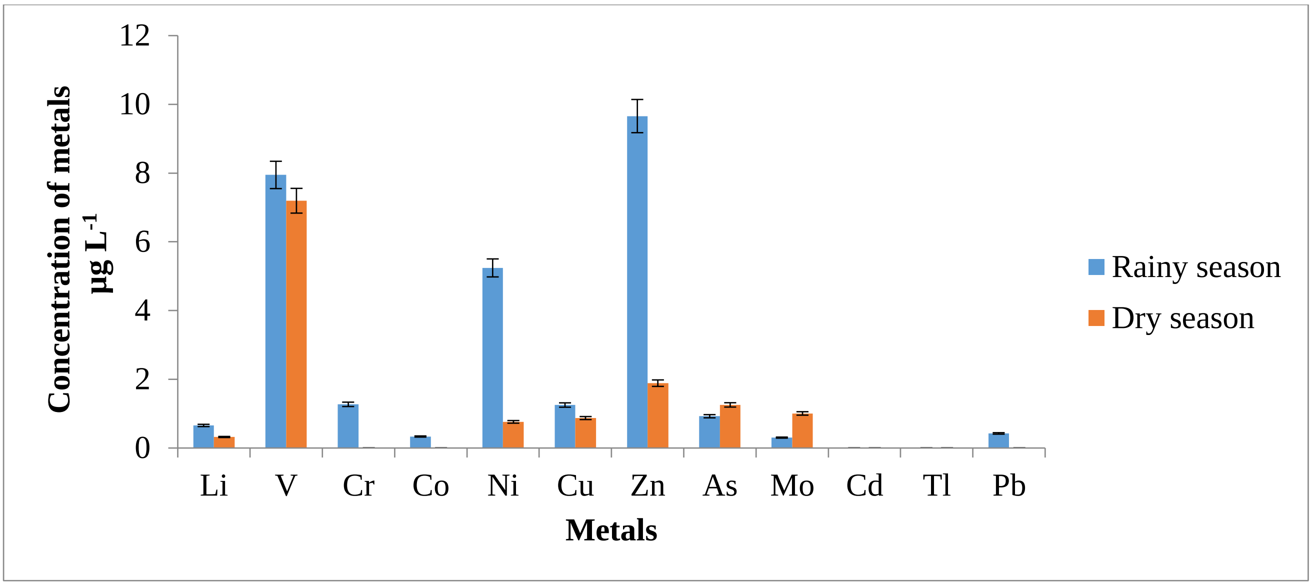

Figure 4.25: Variation of trace metals concentration in dry and rainy season (% SD, n = 3) in sample 7 of Nwanedi river

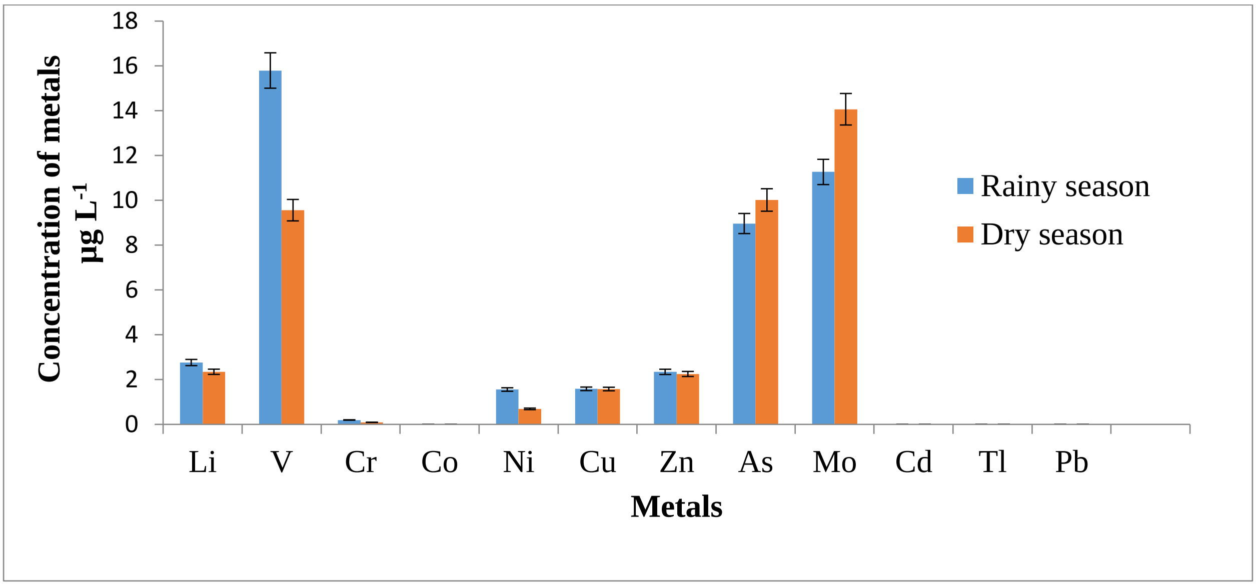

Figure 4.26: Variation of trace metals concentration in dry and rainy season (% SD, n=3) in sample 8 of Tshipise river

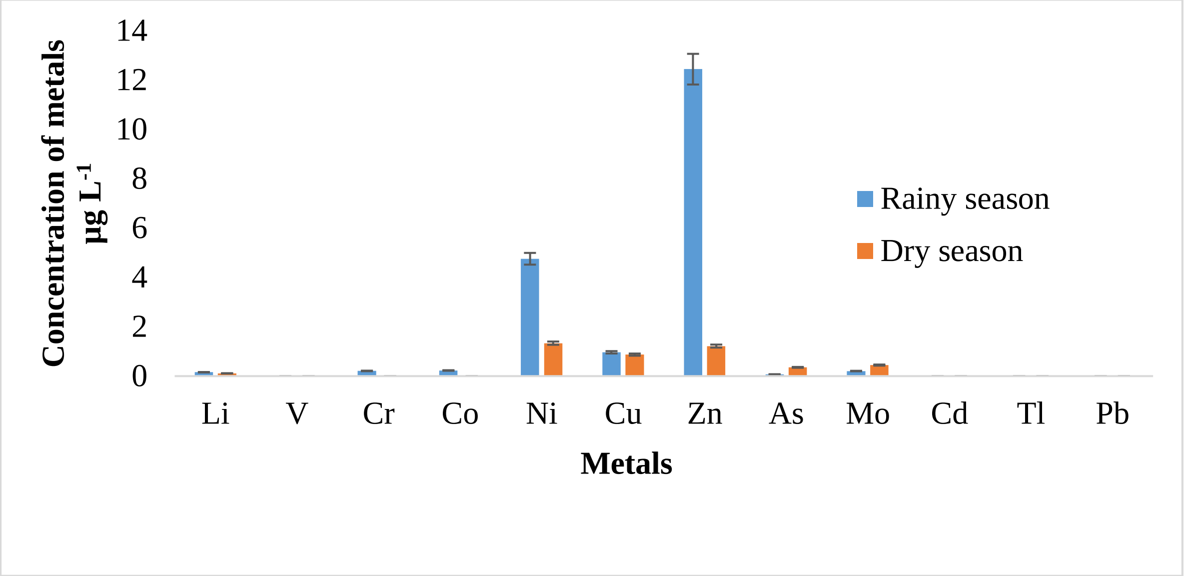

Figure 4.27: Variation of trace metals concentration in dry and rainy season (% SD, n = 3) in sample 9 of Nwanedi river

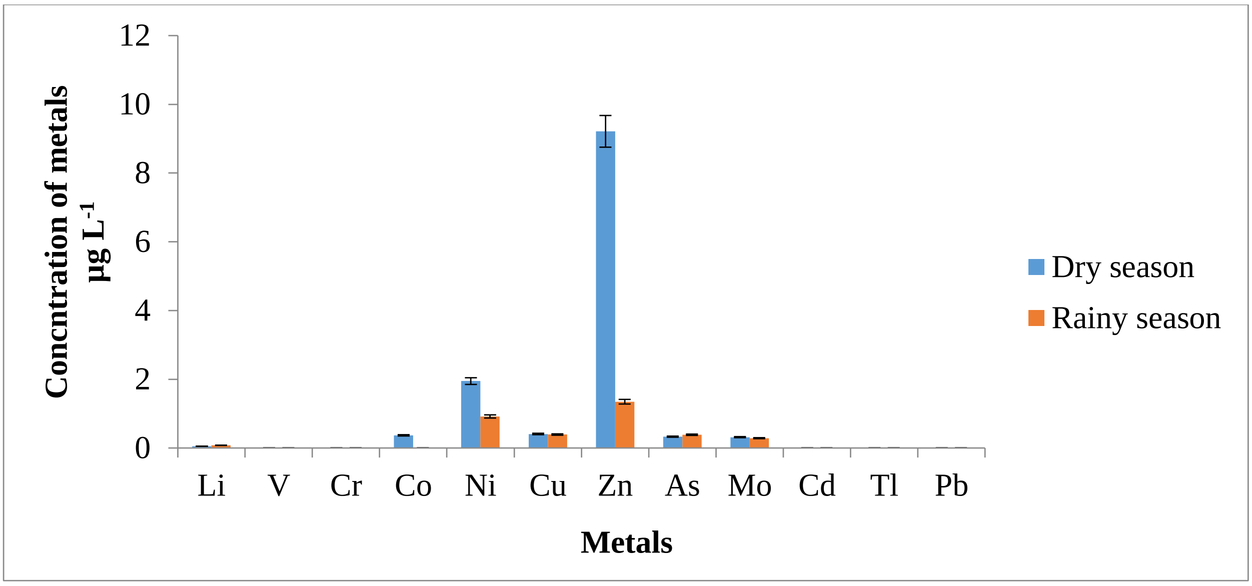

Figure 4.28*:* Variation of cations concentration in a dry and rainy season (% SD, n = 3) in sample 10 of Nzhelele river

Chapter 5: Conclusions and recommendations

In this chapter, concluding remarks, recommendations and future work are summarised based on the results and discussions.

5.1 Conclusions

Analysis of both anions and cations were carried out and characterized by using IC, ICP-OES and ICP-MS techniques. Analysis of samples revealed that the pH of river samples were neutral, at pH 7. The TDS value was found to be the most influential factor affecting the quality of water and the presence of most ions in water. The TDS, anions and cations results, however, displayed a pattern of behaviour associated with anthropogenic sources such agricultural activities and natural occurring ions. Tshipise river was found to be the most contaminated river than all other rivers. Tshipise river had high EC, TDS values and high concentrations of Cl^-, SO_4^{2-}, F^-, Mg, Na, Fe and As which did not comply with the recommended values of WHO, SANS and Canadian drinking water quality. Tshipise river also contained very hard water during rainy season. The second most contaminated river was Nwanedi river, which had slightly high EC, TDS values, conversely contained concentration of Fe that exceeded the MAL of drinking water. Mutale and Nzhelele rivers were also found to be contaminated with Fe. The order abundance of cations and trace metals in the river samples is as follows Na > Mg > Ca > K > Fe >Al and Zn > V > Mo > As > Ni > Co > Cr > Cu > Li > Pb respectively. Whereas the order of anions is as follows $SO_4^{2-} > Cl^- > NO_3^- > F^-$. There were variations on the concentrations of all ions as the season changes. There was no consistency in the increasing and decreasing of both anions and cations in a season. Some of the concentration of anions decrease in rainy seasons, whereas some were increasing in dry season. However, rainy season the concentrations of Al, Li, V, Cr, Ni, Cu, Zn, Al, Ca, Mg, K and Na were high in all river samples. Hence, most ions and metals were high during rainy season. It is then concluded that as the season changes the concentration of both anions and cations also changes. Nwanedi and Tshipise rivers water were found to be unsuitable for use for irrigation.

5.2 Recommendations

- High concentration of TDS, EC and other parameters raises significant environmental concern and calls for urgent attention and appropriate response as the community are depending on the water for survival.
- Municipality have to do community awareness and educate people on effects of water pollution.
- Affordable water treatment system must be implemented before the community use water (filtration method and reverse osmosis), to remove of hazardous ions.

5.3 Future work

- Although this study focused on environmental monitoring of total concentration of metals and ions, with the findings (concentrations of As in Tshipise river), it is of importance to continue with such a study on acid mine drainage and speciation.
- Because the scope of this study was on anions and cations in water, some important factors may not have been given full consideration. In the future, a comprehensive study regarding trace elements on leaching work of soil should be carried out, wherein adsorption and absorption of metals in the soil will be considered.

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7.0 Appendix

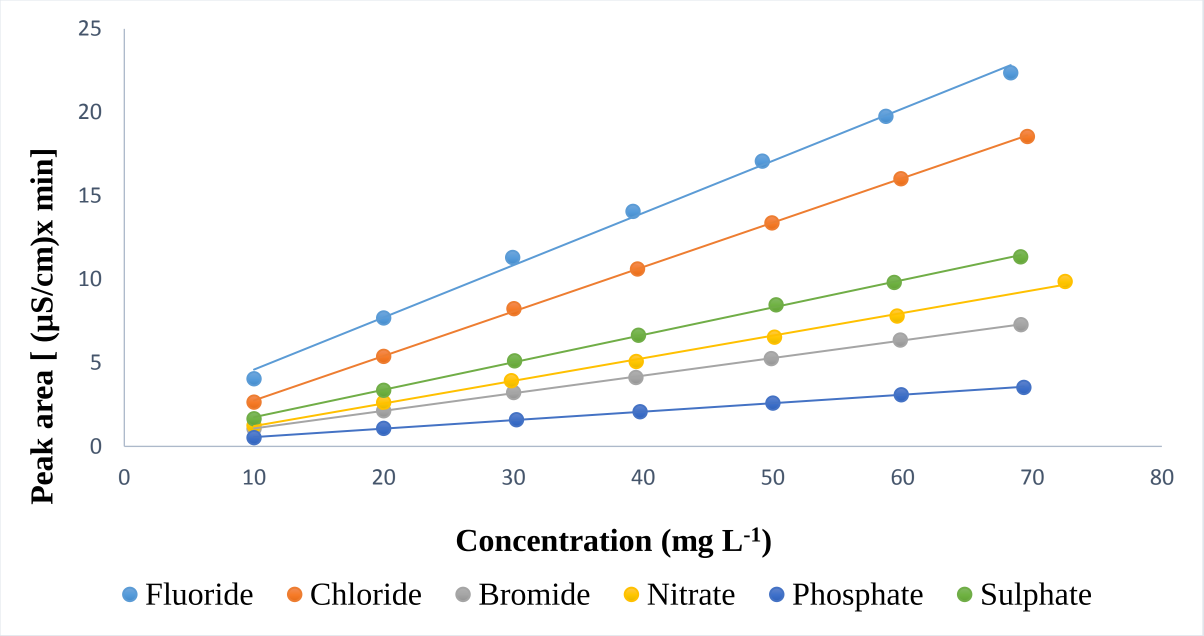
A-1: Sampling point

The picture showing Nzhelele river (picture taken by the author).

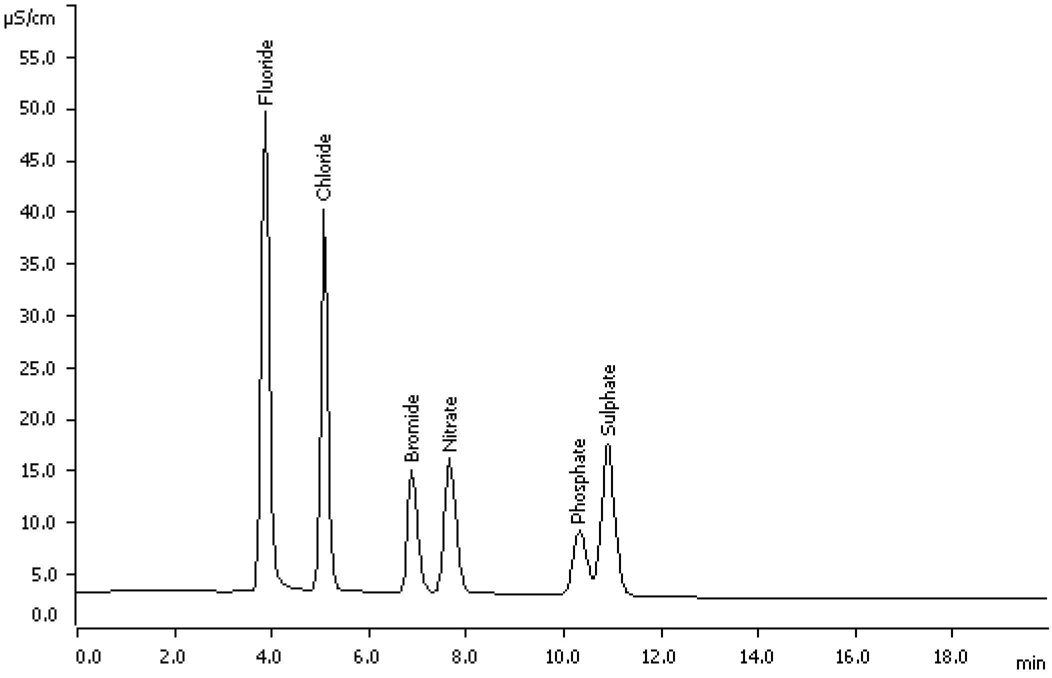
A-2: Correlation coefficient, retention time, linearity equations obtained by using ion chromatography

Anion	Correlation coefficient (R^2)	Linearity equation	Retention time (RSD)	Peak area precision (RSD)
Fluoride	0.9964	Y=0.3125x+1.4738	0.0304	6.5620
Chloride	0.9998	Y=0.2662x+0.0919	0.0216	5.7198
Bromide	0.9994	Y=0.1642x+0.1085	0.0107	2.2526
Nitrate	0.9985	Y=0.1354x-0.1382	0.0082	3.0039
Phosphate	0.9998	Y=0.1054x+0.0230	0.0271	1.0878
Sulphate	0.9995	Y=0.0508x+0.0483	0.0113	3.4910

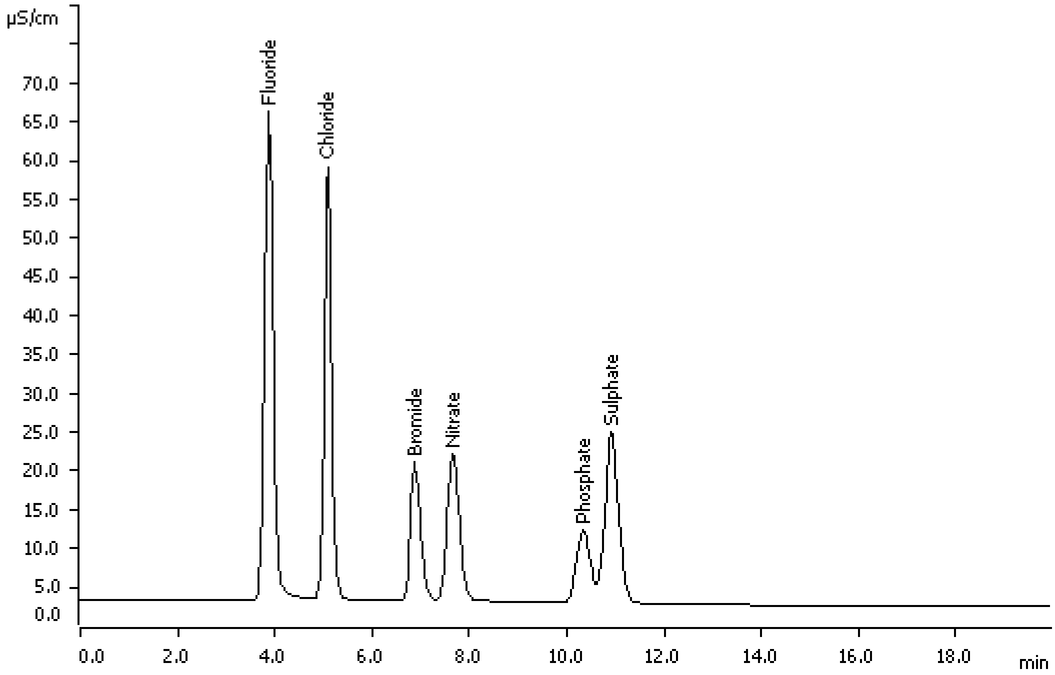
A-3: Calibration curves of anions standards generated from linear range data (10 to 70 mg L^{-1}) prepared for dry season analysis.



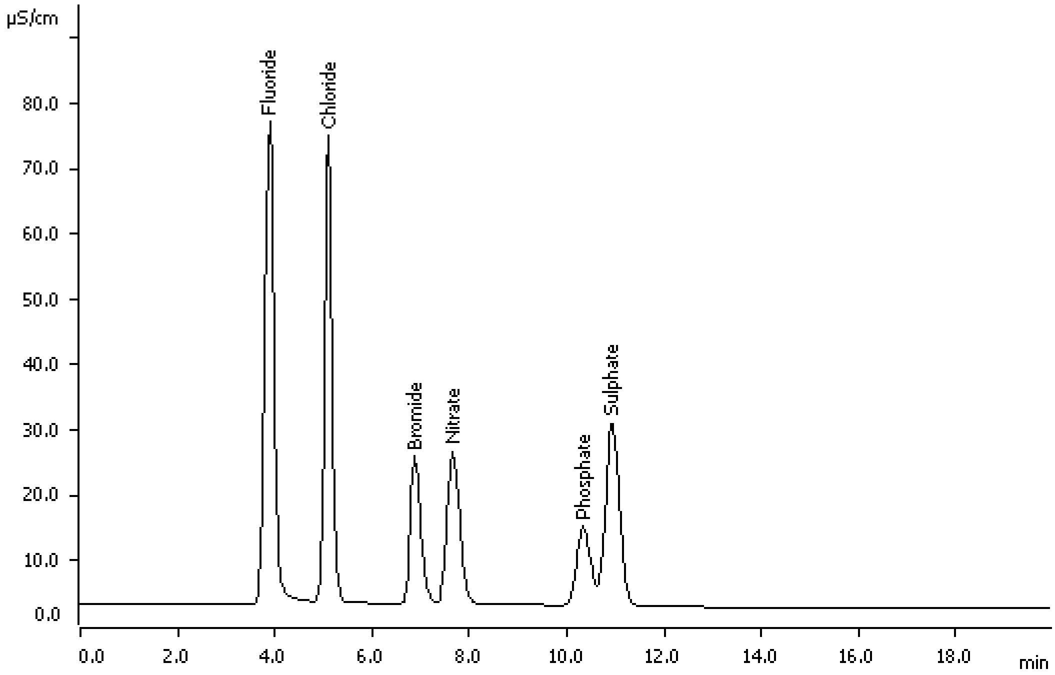
A-4: Chromatograms of standards



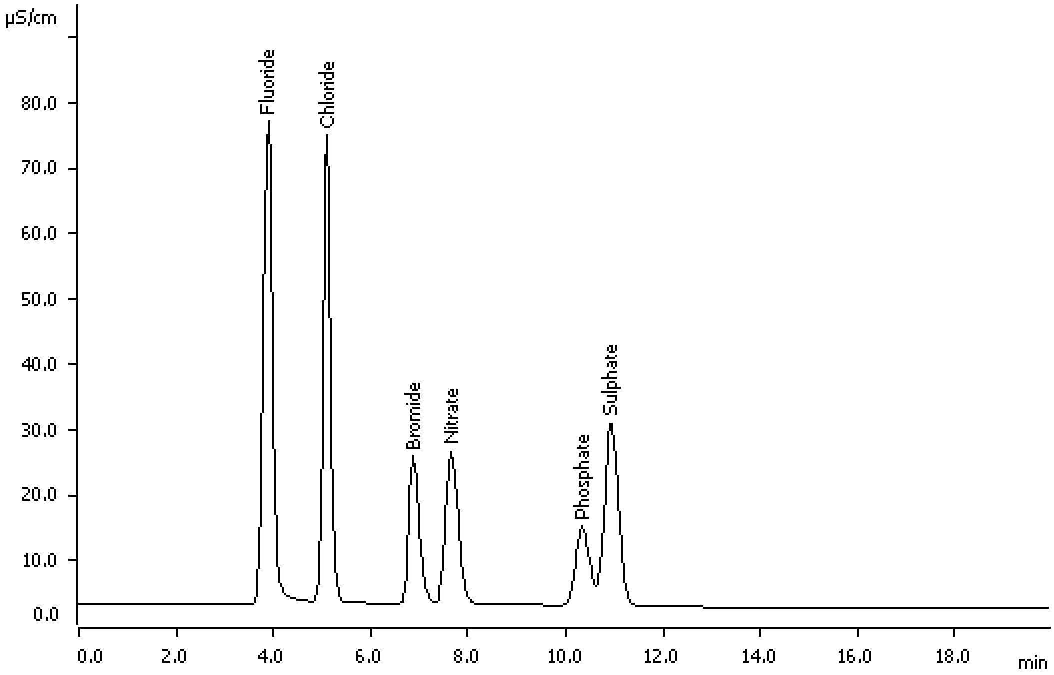
20 mg L^{-1} chromatogram



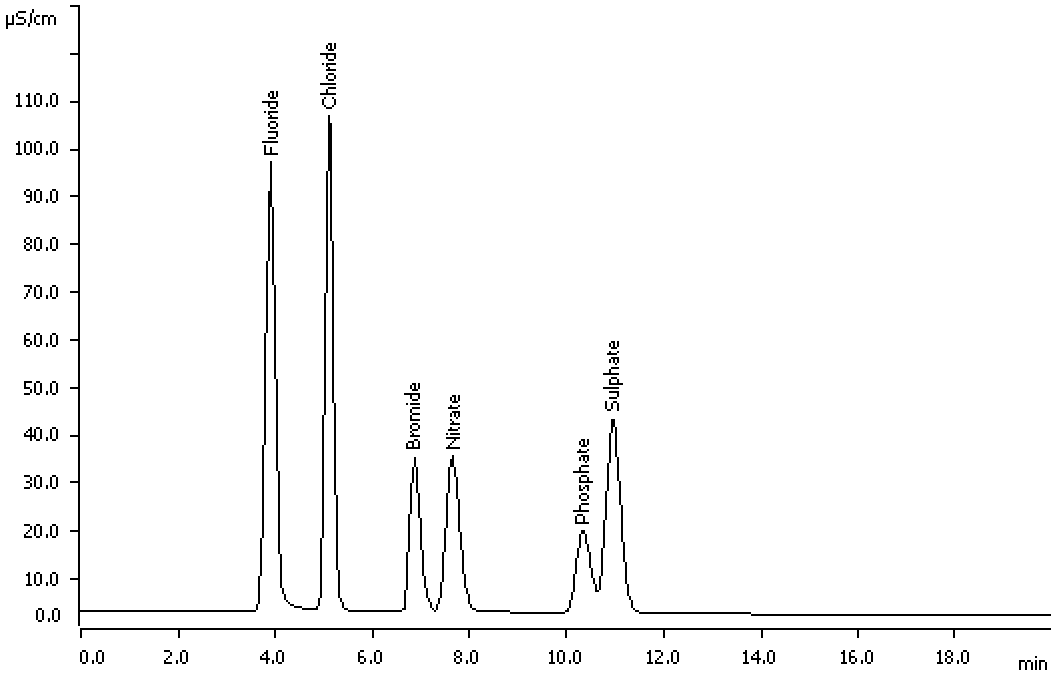
30 mg L^{-1} chromatogram



40 mg L^{-1} chromatogram

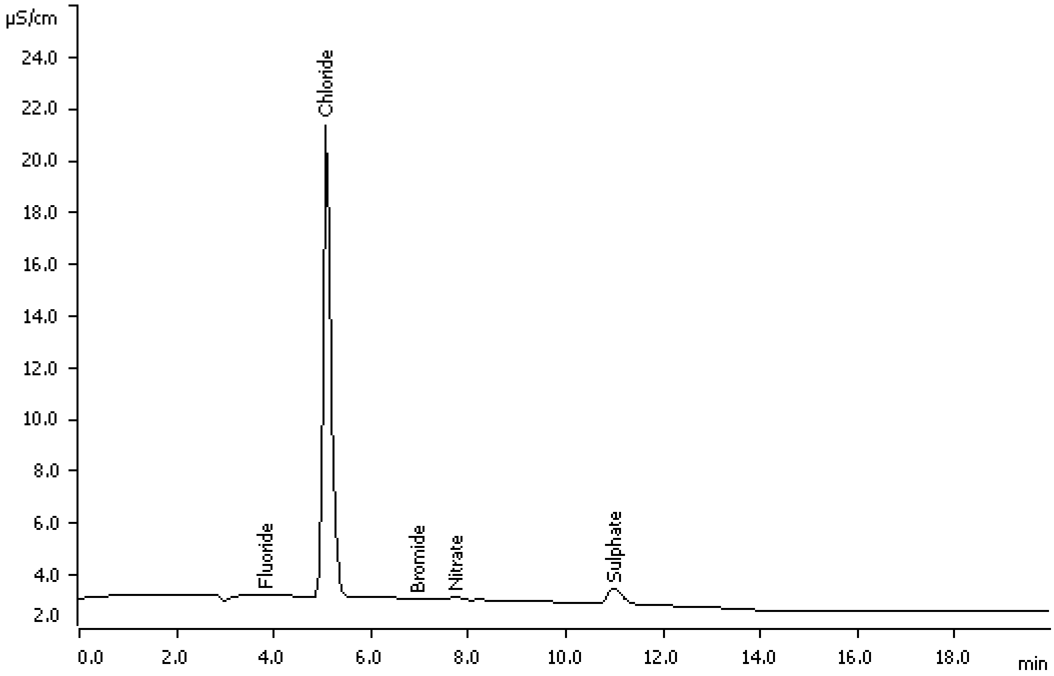


50 mg L^{-1} chromatogram

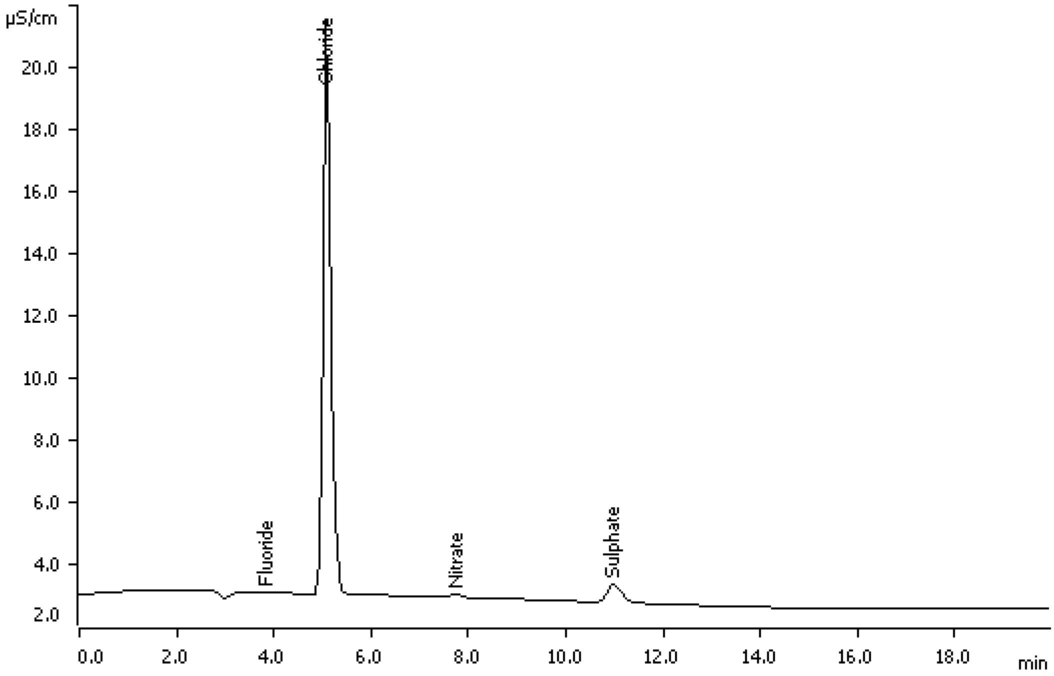


60 mg L^{-1} chromatogram

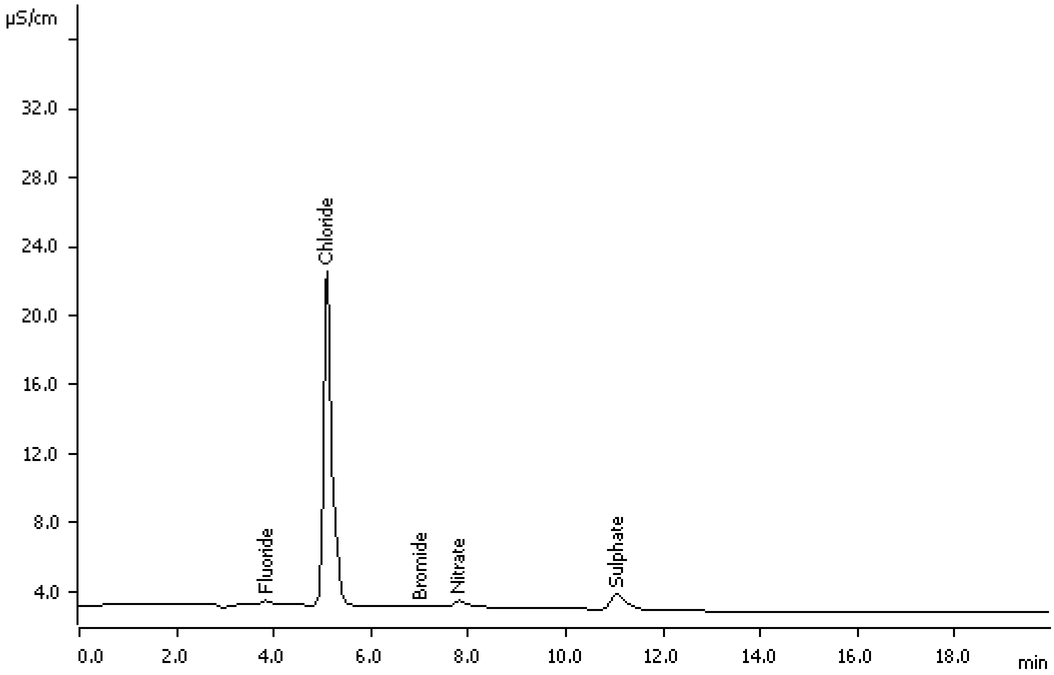
A-5: Chromatograms of samples



Mutale sample chromatogram



Nwanedi sample chromatogram



Nzhelele sample chromatogram