HYDROGEOCHEMICAL MODELLING AND ISOTOPIC COMPOSITION AS TRACERS OF GROUNDWATER RECHARGE IN CHITIPA DISTRICT, MALAWI

MASTER OF SCIENCE DEGREE IN WATER RESOURCES MANAGEMENT AND DEVELOPMENT

WATSON MWAISEN KABAGHE

MZUZU UNIVERSITY

JULY 2024

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A THESIS SUBMITTED TO THE FACULTY OF ENVIRONMENTAL SCIENCES OF MZUZU UNIVERSITY IN FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF A MASTER OF SCIENCE DEGREE IN WATER RESOURCES MANAGEMENT

MZUZU UNIVERSITY

JULY 2024

DECLARATION

I hereby declare that this thesis titled," *Hydrogeochemical Modelling and Isotopic Composition as Tracers of Ground Water Recharge in Chitipa district*, *Malawi*" has been written by me and is a record of my research work. All citations, references, and other people's work have been duly acknowledged. It is being submitted in fulfilment of the requirements for the award of the Master of Science Degree in Water Resources Management and Development at Mzuzu University. None of the present work has been submitted previously for any degree or examination in any other University.

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Signature…… Date……..……

CERTIFICATE OF COMPLETION

We, the undersigned, certify that this thesis is a result of the author's work, and that to the best of my knowledge, it has not been submitted for any other academic qualification within the Mzuzu University or elsewhere. Further the thesis is acceptable in form and content, and satisfactory knowledge of the field covered by the thesis was demonstrated by the candidate through an oral examination held on 10th June, 2024.

…….. ……

Associate Professor Elijah Wanda (PhD.) **Date**

(Supervisor)

…… …...……

Dr. Russel Chidya (PhD) **Date**
(Co-supervisor)

…….. ……

Dr. Russel Chidya (PhD) **Date**
(Postgraduate Coordinator)

…… …….

Dr. Brighton Chunga (PhD.) **Date**

(Head of Department)

ABSTRACT

This study aimed to assess the hydrogeochemical and isotopic composition of groundwater as tracers of recharge in Chitipa district. The study area faces challenges of water scarcity and understanding the mechanism of groundwater recharge is critical for sustainable water resource management and planning. Field surveys were conducted in Traditional Authorities (TAs) Mwaulambya and Mwenemisuku during which groundwater samples were collected from 25 randomly selected boreholes in dry and wet seasons. Two sets of triplicate samples were collected at each water point in October 2021 and April 2022; a non-acidified and an acidified pair for anion and cation analyses, respectively. A replicate for stable isotope analysis was also collected. Hydrochemical analysis involved the determination of major cations, anions, and physical parameters. Stable isotope analysis included deuterium (δ^2H) and oxygen-18 ($\delta^{18}O$). Data analysis was done using SPSS version 20. Student's t-test was used to examine seasonal changes in groundwater composition and the hydrochemical data was validated using ionic balance error (IBE) as part of quality control and assurance. The study revealed the following: There is a significant difference ($p< 0.05$) in levels of electrical conductivity (EC), nitrate (NO_3^-), chloride (Cl^-), bicarbonate (HCO_3^-), potassium (K^+), and calcium (Ca^{+2}) and no significant difference ($p > 0.05$) in levels of pH, sodium (Na^+), sulphate (SO_4^{-2}) and magnesium (Mg^{+2}) between the dry and wet seasons. The stable isotope composition showed that the groundwater provenance is of meteoric origin, and likely of recent precipitative recharge. The hydrochemical modeling showed that aquifers in the study area are predominantly rocks rich in alkali metals, bicarbonate, and chloride minerals, whereas 40% of the boreholes showed prevalence of alkali earth metals. Gibbs diagram revealed groundwater evolution dominated by the dominance of rock weathering as a predominant process controlling the groundwater chemistry. Ionic dominance sequence analysis coupled with Piper plots showed that groundwater in the study area is mainly of mixed types, namely Ca-Na-HCO_3 and Ca-Mg-SO_4. Overall, the ionic dominance sequence was in the following order: $Na^+ > Mg^{+2} > Ca^{+2} > K^+$ for cations, and $HCO_3^- > Cl^- > SO_4^{-2} > NO_3^-$ for anions, both during the dry and wet seasons. The groundwater quality of all the boreholes was found to be within the recommended WHO guidelines and complied with the Malawi Standards for drinking water from boreholes (MS733:2005). The findings of this study recommend: The sustainable utilization of groundwater resources and the intensification of effective recharge enhancement strategies such as afforestation, proper agricultural practices, and building pit latrines per established sanitary practices.

ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectrometry
CRD	Completely Randomized Design
GMWL	Global Meteoritic Water Line
GoM	Government of Malawi
GVH	Group Village Head
GMS	Groundwater and Mineral Services
GCS	Council for Geosciences
HDPE	High-Density Polythene
IWRM	Integrated Water Resources Management
MS	Malawi Standards
MZUNI	Mzuzu University
NGO	Non-Governmental Organization
SGDs	Sustainable Development Goals
SPSS	Statistical Package for Social Science
SEP	Social Economic Planning
QRD	Quantitative Research Design
TA	Traditional Authority
UN	United Nations
UNILIA	University of Livingstonia
WHO	World Health Organization

DEDICATION

I dedicate this work to my late mother – the most incredible woman I knew and loved.

ACKNOWLEDGEMENTS

I would like to express my heartfelt appreciation to my primary supervisor, Associate Professor Elijah Wanda (PhD), and co-supervisor Dr. Russel Chidya (PhD), for their unwavering support, insightful guidance, and invaluable feedback throughout the entire research process. Their expertise and encouragement were instrumental in shaping this work.

I am deeply grateful to my colleagues at the University of Livingstonia whose financial, moral, collaborative spirit and constructive feedback greatly enriched the development of this thesis.

Further, I extend my thanks to the dedicated personnel at Central Water Laboratory, especially Mr. Anold Zavison, who assisted with various technical aspects of this research such as hydrochemical and isotopic analysis, and thanks to Mr Chikumbusyo Kaira and Limbikani Banda.

To my family, I owe a debt of gratitude for their patience, understanding, and unwavering support during the ups and downs of this academic journey. Their encouragement provided the much-needed emotional anchor throughout this process.

Lastly, I extend my thanks to all those who, in ways both big and small, contributed to the completion of this thesis. Your support has been invaluable.

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CHAPTER ONE: INTRODUCTION

1.0 Background information

The significance of water for the sustenance of life cannot be overemphasized. Water has been an agent for development, catalyzing the advent and proliferation of civilizations throughout the course of history (United Nations, 2008). This is currently evident in the fact that access to clean water and sanitation for all is the post-2015 sustainable development goal (SDG) number 6 (UN, 2015a). Water is also an essential medium for life in both natural and artificial aquatic ecosystems, which face adversity for long periods because of its low quantity and quality levels.

Globally, groundwater and surface water are the major sources of water for domestic, agricultural, and industrial use. Approximately one-third of the world's population uses groundwater for domestic purposes (Nickson *et al.,* 2017). Current aquifer recharge rates are a fundamental consideration for the sustainability of groundwater resource development. Moreover, understanding aquifer recharge processes and their linkages with land use is essential for integrated water resources management (IWRM). Groundwater recharge and groundwater flow processes are generally controlled by climate, morphology, and geological conditions (de Vries and Simmers, 2002; Gleeson and Novakowski, 2009). Research studies have been done to investigate groundwater recharge and groundwater flow processes in various climatic regions and geological media, particularly those with a combination of permeable rock matrices and conductive fractures (Chilton and Foster, 1995; Apaydin, 2010; Monjerezi *et al*., 2011; Roques et al., 2014; Verbovsek and Kanduc, 2016). Groundwater composition properties are defined by hydrogeochemical processes of solutions or precipitation of solid minerals, reduction and oxidation of compounds, dissolution or evolution of gases, sorption or ion exchange, pollution, leaching fertilizers or manure, and mixing of different waters (Tikhomirov, 2016). Hydrogeochemical processes depend on water and rock interaction, atmospheric inputs, chemical inputs from human activities, precipitation, geological structure, and the mineralogy of aquifers (Blanchette et al., 2013).

Hydrogeochemistry is an essential tool for the verification of conceptual models, especially groundwater flow models. According to Blanchette *et al.* (2013), these are largely controlled by physical and chemical interactions occurring within the aquifer system, which are responsible for seasonal and spatial variations of groundwater chemistry and quality. The complexity of the hydrogeochemistry of the aquifers can be understood through an

understanding of geochemical processes, major ion chemistry, and local geology. Such major geochemical processes within basement aquifers are ionic exchange, evaporation and dissolution of carbonates, gypsum, and silicate weathering (Postma *et al*., 2008). Worldwide water resources are facing threats due to pollution, which need traces and hydrogeochemical models to investigate. Environmental isotopic and hydrochemical investigation techniques provide much information on groundwater flow systems and the main hydrogeochemical processes affecting the composition of water (Limbikani *et al.,* 2019). Water-isotope tracing is a powerful tool for conceptualizing hydrological systems, including the characterization of hydrological conditions, flow-system evolution, groundwater and surface water exchange, groundwater recharge, and water source provenance (Araguas and Yurtsever, 2008).

Recent studies have shown that isotopic traces are widely used in tracing pollution worldwide. Evidence indicates that the stable environment isotopes of oxygen-18 ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) are excellent tracers for determining groundwater origins (Jin *et al.,* 2016). This stems from the fact that their concentrations are usually not subject to change by interaction with the aquifer material. In a study conducted in East African aquifer systems, researchers using these isotopes investigated the main recharge source of the Nairobi aquifer system (Oiro *et al.,* 2018). Isotopic data characterization techniques have become well-established in the hydrological society for groundwater resource assessment, development, and management and are now an integral part of many water quality and environmental studies (Brikle and Bundschuch, 2007). Stable isotopes are excellent indicators of the circulation of water; they reflect the origin of the water and the processes of recharge (Jin *et al.*, 2016). In Malawi, isotope data has been employed to study groundwater recharge sources in Chikwawa district (Monjerezi *et al*., 2011).

In Malawi, groundwater is the main source of drinking water in most rural areas due to the scarcity of surface water (GoM, 2005). As such, the Malawi Water Resources Act (2013) emphasizes the quantity and quality of water for basic human needs and the protection of aquatic ecosystems, securing ecologically sustainable development. Several studies have articulated the need to investigate groundwater pollution with the use of isotopes in the water. Saka et *al*. (2011) narrate that the water isotopes ($\delta^{2}H$ and $\delta^{18}O$) are excellent tracers for determining the origin of groundwater and are widely used in studying natural water circulation and groundwater movement due to their conservative characteristics of moving with the water molecule. In addition, such studies help in the development of a hydrogeological model. Wanda *et al.* (2013) indicate that without a well-defined hydrogeological model, sustainability in food

production cannot be achieved. Chitipa's aquifer systems primarily consist of fractured crystalline rocks and sedimentary formations. These aquifers are vital for supplying water to the region for various purposes, including agriculture, domestic use, and industry. Proper management and conservation of these aquifers are crucial for ensuring a sustainable water supply in Chitipa. Therefore, the research aims to assess the hydrogeochemical and isotopic composition of groundwater as a tracer of recharge in the Chitipa district.

1.1 Problem Statement

Groundwater accessed from boreholes and shallow wells is a major source of domestic water in semi-urban areas of Malawi, such as Chitipa district. Pollution of the water is one of the main problems affecting groundwater quality in Malawi (Chidya *et al.,* 2016). Water from these sources can be polluted by chemical and biological agents, leading to the occurrence of water-related diseases. This may occur at the point of use or the source due to natural or anthropogenic factors (Pitchard *et al.,* 2009). Pollutants in groundwater aquifers, if undetected, cannot be removed from the water, and when ingested through drinking water or cooked food, may cause diseases and increased mortality after bioaccumulation in body tissues. Identification of potential sources of groundwater pollutants is key to abating the pollution. This involves establishing the groundwater recharge processes.

There is limited data on groundwater quality in the reviewed literature for Chitipa district in Malawi. Nevertheless, climate change and population growth are reported to have impacted the supply of potable water within the district (Chitipa Social Economic Plan, 2017). The rapid increase in agricultural and other activities due to population growth has led to a deterioration of water quality and quantity in the district (SEP, 2017). The unavailability of water quality data limits the application of water resource preservation and conservation practices such as afforestation to address the problem of groundwater quality. Hydrogeochemical and isotopic tracers are viable tools for monitoring water quality and identifying the source(s) of groundwater recharge (Jin *et al.*, 2016). Identification of possible groundwater sources provides remedial action to protect water resources from pollution and promote human health.

This study therefore aimed at utilizing hydrogeological modeling and isotopic composition as tracers of groundwater recharge in Chitipa district.

1.2 Objectives

1.2.1 Main Objective

To assess the hydrogeochemical and isotopic composition of groundwater as tracers of recharge in Chitipa district.

1.2.2 Specific Objectives

The specific objectives of this study were:

a) To characterize the hydrogeochemical-stable isotopic composition ($\delta^{2}H$ and $\delta^{18}O$) of groundwater in Chitipa district.

b) To assess changes in the hydrogeochemical and isotopic composition of groundwater with seasons in Chitipa district.

c) To determine groundwater recharge sources such as precipitation, and infiltration in Chitipa district.

d) To examine the hydrogeochemical processes that govern groundwater quality in Chitipa district.

1.3 Research Questions

The Research questions of the study are:

a) What are the magnitudes of hydrogeochemical and stable isotopic compositions of groundwater in Chitipa during the wet and dry seasons?

b) What are the recharge sources of groundwater in Chitipa?

c) What are the groundwater types characterizing the groundwater system, and which water type is dominant in Chitipa?

d) What are the major hydrogeochemical processes controlling groundwater evolution in Chitipa?

1.4 Significance of the Study

The study delineates groundwater recharge sources, thereby informing policy on catchment and groundwater resource management aspects. The findings are informing various

stakeholders (e.g., health experts, NGOs, and environmental managers) in the water sector on IWRM and sustainable management of water resources in the district. It is also providing data on the state of groundwater quality in the district. With this data, mitigating factors for preservation and conservation practices may be adapted or adopted for water sources in the district. This is because understanding the characterization and hydrochemistry of the aquifers contributes to the management of the quality and quantity of groundwater resources (Bank and Joloza, 2020). The local population is benefiting from the informed decisions that the government and its partners make in the provision of good-quality water in sufficient quantity. The study contributes to a better understanding of the groundwater system in the district and will form a foundational basis for future hydrogeological studies in the region.

CHAPTER TWO: LITERATURE REVIEW

2.0 Introduction

This chapter presents what is currently known and what has been researched before about the problem under consideration. It sets the scholarly context for the question or hypotheses of the proposed study. In addition, it helps the researcher to fit in with the existing body of knowledge.

2.1 Groundwater

Groundwater is becoming a vital water resource for domestic use, ecosystem health, and economic development in most sub-Saharan African regions and arid and semi-arid countries due to global population growth (Luo *et al.,* 2018). However, groundwater resource availability can be effectively utilized and sustained if the quantity and quality are well defined. Climate, geomorphology, geology, hydrogeology, and human activities influence the quality and chemical composition of groundwater (Blanchette *et al.,* 2013). According to Bank and Joloza (2013), groundwater resource management is a critical area of concern and crucial to sustain due to the increasing depletion of water resources caused by an ever-growing population. An understanding of the hydrological and hydrochemical properties of the aquifer is required in the management and evaluation of groundwater resources.

The hydrochemistry of groundwater is a vital indicator and provider of information in assessing environmental conditions (Edmunds and Shand, 2008). Knowledge of the spatial distribution of chemical elements and the influence of anthropogenic factors on groundwater is required to be understood to protect against groundwater contamination. The movement of inorganic and organic chemical species is governed by the natural occurrence of free ions, complexes, or molecules and physical, chemical, and hydrogeological features within the aquifers (Alilouch *et al.*, 2017).

2.1.1 Hydrogeochemistry of groundwater

The quality of groundwater is well explained by its physical, chemical, and biological characteristics, as well as its composition (Aral and Taylor, 2011). Chemical characteristics include inorganic constituents such as salts, nutrients, trace elements including metals, and organic constituents such as benzene, pesticides, and organic carbon. A combination of the composition of water that enters the aquifers and the reactions with minerals present in the rocks results in the chemical composition and characteristics of groundwater (Edmunds and

Shand, 2008). The physicochemical parameters of water quality for groundwater are temperature, turbidity, color, taste, and odor, while biological characteristics constitute the pathogen indicator organisms such as protozoa, bacteria, and viruses (Chen *et al.,* 2019)

Groundwater quality is concerned with health risks, ecological impacts/ecosystem services (hypoxia), industrial uses, aesthetics, agriculture use, operation of the water system, and impacts on aquifer properties (Vasanthavigar *et al.,* 2010). Though groundwater is viewed as the cleanest water source, it tends to be contaminated by several sources. The most common groundwater contaminants are naturally occurring, point sources, and non-point sources (Edmunds and Shand, 2008). Point sources of pollution include leaking underground storage tanks (gas stations), industrial spills, landfills, septic systems, sewer lines, animal feedlots, manure lagoons, and leach fields, among others, while non-point sources of pollution include urban runoff and agricultural activities (Aral and Taylor, 2011).

Groundwater sampling is done for several reasons. Among them is to assess its suitability for industrial, irrigation, and domestic uses (Weaver *et al.,* 2007). Furthermore, groundwater sampling is done to determine hydrochemical data for an area and to understand the hydrogeology of an aquifer. This aims at understanding recharge, flow, water-rock interactions, and discharge processes (Edmunds and Shand, 2008). Groundwater sampling is also done to investigate groundwater pollution through the identification and quantification of the occurrence of pollutants as well as processes around events. Sampling can also be vital in regular checks to identify changes in the aquifers due to pollution, climate change, and overexploitation. This can be achieved through the random collection of samples and regular observations (Weaver *et al.,* 2007).

2.1.1.1 Temperature

Water temperature is a measure of the kinetic energy of water and is expressed in degrees Fahrenheit (F) or Celsius (C). Water temperature varies according to season, depth, and, in some cases, time of day (Twort *et al.,* 2000). Temperature is also important because it influences the chemistry of water. The rate of chemical reactions generally increases at high temperatures. Water, particularly groundwater, with higher temperatures can dissolve more minerals from surrounding rocks and will therefore have a higher electrical conductivity (Ayobahan *et al.,* 2014).

2.1.1.2 pH

The pH is the log of the reciprocal of the hydrogen ion (H^+) concentration (Drawbored, 1999). The pH scale ranges from 1 to 14, where pH signifies the equal concentration of H^+ and hydroxide (OH^-) ions. The lower values indicate that water is acidic, which may lead to corrosion of metallic pipe distribution systems (Twort *et al.,* 2000) and the dissolution of heavy metals in the substrata of water bodies, which are toxic to both humans and aquatic life. Values higher than 7 show that the water is basic, and there is limited information on the health and ecological effects of elevated pH. WHO (2008) and MS (2013) recommend pH values of 6.5–8.5 for drinking water.

2.1.1.3 Electrical conductivity

Electrical conductivity (EC) is a measure of the ability of water to conduct electricity with components dissolved therein (DWAF, 1996). This parameter (measured in micro-Siemens per centimeter (*Scm-1)*) is directly proportional to total dissolved solids, and the Malawi Standards (MS733:2013) recommend a maximum EC of 3500 μS/cm on health grounds concerning the adverse impacts on infants, heart patients, and individuals with renal disorders (Crawford *et al.,* 1999). High levels of electrical conductivity in water can also impart a bitter taste, compromising the aesthetic quality of the water.

2.1.1.4 Total Dissolved Solids

The mineral components dissolved in water comprise dissolved solids. The concentration of dissolved solids in natural water is normally less than 500 mg/L, and hence water with a concentration a concentration greater than 500 mg/L is unsuitable for drinking and many industrial uses (WHO, 2008). Therefore, the total concentration of dissolved minerals in water is a universal indication of their overall suitability for various uses. The high TDS concentration in groundwater may be due to the occurrence of bicarbonates, carbonates, sulfates, chlorides, and calcium (Monjerezi and Ngongondo, 2012). The methods that remove TDS are reverse osmosis, electrodialysis, exchange, and the solar distillation process (Ayobahan *et al.,* 2014). A high value of TDS influences the taste, hardness, and corrosive properties of the water source. The TDS is of great significance in determining the quality of water, as it indicates the hardness of the water (source). Due to differences in the solubility of minerals, TDS in water varies significantly in different geological regions (Monjerezi and Ngongondo, 2012).

2.1.1.5 Sodium

Sodium (Na^{+}) is an alkali metal that is found in natural waters underlain by plagioclase and/or forms hornblende (Bell, 2007). It is a constituent of common table salt and is also naturally found in association with chloride ions. Excessive intake of sodium can cause heart disruption in infants and water balance in the body as it influences the function of the kidneys (Crawford *et al.,* 1999). Furthermore, in association with chloride ions, sodium can impact a salty taste, altering the aesthetic quality of water (DWAF, 1999). The MS (2013) and WHO (2008) recommend Na concentrations of 100–200 and 200 mg/L on both aesthetic and health grounds (WHO, 2008).

2.1.1.6 Potassium

Potassium (K^{+}) is another alkali metal found in low concentrations in natural waters since rocks that contain potassium are relatively resistant to weathering. However, potassium salts are widely used in industry and fertilizers for agriculture and enter freshwaters with industrial discharges and run-off from agricultural land (Chapman, 1996). Potassium is an essential element in humans, and is seldom, if ever, found in drinking water at levels that could be a concern for healthy humans (Twort *et al.,* 2000). The drinking water standards set by the World Health Organization recommend a limit of 50 mg/L (WHO, 2005).

2.1.1.7 Calcium

Calcium (Ca^{+2}) is an alkali earth metal that is present in water, usually from calcareous underlying rock structures. It is present in association with carbonates (Twort *et al.,* 2000). The most common source of calcium in groundwater is through the erosion of rocks, such as limestone and dolomite, and minerals like calcite. The source of this element in groundwater is calcite, which is the major contributor to the hardness of the water. Though hard water is not a health hazard, it can be a nuisance in homes (Suleiman *et al.,* 2013). One other importance of calcium in groundwater is its ability to block the absorption of heavy metals in the body and its ability to increase bone mass and prevent certain types of cancer.

2.1.1.8 Nitrate

Nitrate (NO3) is an inorganic anion that occurs under a variety of conditions in the environment, both naturally and synthetically (McClelland and Trautmann, 2012). Natural sources of nitrate include mineral deposits, soils, and the atmosphere. Elevated levels can be

attributed to decaying organic matter, but also to human and animal wastes, industrial discharges, and fertilizers. Higher levels are often found in shallow aquifers easily polluted by sewage and fertilizer applications. Nitrite is closely associated with nitrate because it quickly oxidizes to nitrate. It is further stated that a high concentration of nitrate converts hemoglobin, or blue baby disease, where oxygen is not transported. High concentrations of nitrogen are a threat to human health.

2.1.1.9 Magnesium

Magnesium (Mg^{+2}) is an alkaline metal that is naturally present in water from underlying rock structures (Crawford *et al.,* 1999). Magnesium is a relatively abundant element in the earth's crust, ranking eighth in abundance among the elements. It is found in all-natural waters, and its source lies in igneous rocks, generally present in lower concentrations than calcium. It is also an important element contributing to hardness and a necessary constituent of chlorophyll (Suleiman *et al.,* 2013). Its concentration greater than 125 mg/L can influence cathartic and diuretic actions.

2.1.1.10 Bicarbonates

Bicarbonates (HCO3) are a natural component of all mineral waters. Mineral waters that are sourced from limestone-rich areas typically have a high bicarbonate content. The fossil carbon of calcite and dolomite in the aquifer would contribute half of the bicarbonate ions. This weathering enriches the groundwater with calcium, magnesium, and bicarbonate ions (Ayobaham *et al.,* 2014). The concentrations of bicarbonate in the groundwater samples range from 39.6 to 183 mg/L. Bicarbonate plays a vital role in buffering acids and ensuring that the mineral water tastes pleasantly clean and refreshing.

2.1.1.11 Carbonates

Carbonate-rich rocks such as limestone, dolomitic limestone, and dolomite are the major starting materials for carbonate weathering. The available carbonates in these rocks are dissolved and added to the groundwater system by way of rainfall, irrigation infiltration, and groundwater movement (Ayobaham *et al.,* 2013). Carbonate serves as a charge-balancing anion (negatively charged ions) for calcium, magnesium, sodium, and other cations (positively charged ions). High bicarbonate and carbonate levels in the presence of calcium and magnesium may lead to the formation of lime deposits in plumbing and irrigation systems.

2.1.1.12 Sulphate

Sulfate (SO_4^{-2}) is present in a minimal concentration in freshwater, with elevated concentrations in brackish and marine waters (Twort *et al.,* 2000). Water containing a high concentration of these anions has a laxative effect on sensitive groups, such that it is predominantly responsible for travelers' diarrhea (Crawford *et al.,* 1999). The reduction of sulfate by bacteria in anaerobic environments also leads to the formation of hydrogen sulfide, which is characterized by a rotten egg odor that disappears with efficient aeration of the water and is also known to possess a corrosive effect on iron-based pipework (Twort *et al.,* 2000).

2.1.1.13 Chlorides

Chloride (Cl) in surface and groundwater comes from both natural and anthropogenic sources, such as run-off containing road de-icing salts, the use of inorganic fertilizers, landfill leachates, septic tank effluents, animal feeds, industrial effluents, and irrigation drainage (Ayobaham *et al.,* 2014). It enters surface waters through the atmospheric deposition of oceanic aerosols and the weathering of some sedimentary rocks (mostly rock salt deposits). High concentrations of chloride can make water unpalatable and unfit for drinking.

2.3 Characterization of environmental water-stable isotopes δ^2H and $\delta^{18}O$ (from different water sources)

The term environmental isotopes refer to isotopes, both stable and radioactive, that are present in the natural environment, either because of natural processes or introduced by humans (Ferranti *et al.,* 2012). Because of their specificity and reliability, environmental isotopes, namely isotopes of lighter elements (hydrogen, carbon, nitrogen, oxygen, sulfur, and chlorine), have more extensively been used to study global element cycles and pollution monitoring (Miljevic and Molobocanin, 2007). Their application to trace the history of specific molecules is based on the different and distinct isotopic composition of the given molecules related to isotopic fractionation in purely physical processes, heterogeneous chemical equilibria, and reaction kinetics caused by their origin and isotopic behavior as they undergo environmental processes such as those involved in transport and the fate of the contaminant in the environment, including evaporation, dissolution, volatilization, sorption, and degradation (Yassine *et al*., 2018).

Environmental isotopes of hydrogen and oxygen are the ideal chemical tracers of water because their concentrations are usually not subject to change by interaction with the aquifer material.

The natural abundance of stable heavy hydrogen (δ^2H) and oxygen-18 ($\delta^{18}O$) isotopes as conservative tracers in water can provide preliminary indications of where it came from and what happened to it on its way there (flow paths and origins of the water) (Miljevic and Molobocanin, 2007). These isotopes are also effectively used for paleo-hydrological studies and delineating the origin of groundwater replenished mainly during the earlier pluvial periods, which is particularly relevant to the occurrence of groundwater in arid regions. Such paleo waters are often characterized by relatively low deuterium excess values in addition to their identification through age dating (Yurtever and Araguas, 1993).

2.3.1 Deuterium (δ^2H)

Deuterium, when injected into the water table, gives direct insight into the movement and distribution of groundwater within an aquifer. Deuterium can be detected in small amounts, informing scientists about where and how much water is flowing in a specific location (groundwater hydrology). Hydrology, using deuterium as a tracer, is applied in environmental studies, water, and waste-water mapping, and more recently in the monitoring of hydraulic fracturing, otherwise known as "fracking" (Miljevic and Molobocanin, 2007). Deuterium is used in hydraulic fracturing in the exploration process for natural gas by oilfield services and applications, as a tracer in drilling fluids (used to determine if drilling fluid penetrated the core), and in geological research (Ferranti *et al*., 2012).

2.3.2 Oxygen-18 ($\delta^{18}O$)

Oxygen-18 ($\delta^{18}O$) is used as a tracer in many hydrologic studies. It is most often used as a component in a mixing model and hydrograph separation, as $\delta^{18}O$ acts conservatively and is applied naturally and uniformly over broad areas (Ferranti *et al.,* 2012). Oxygen-18 ($\delta^{18}O$) can be used when different sources (old water/new water) have different isotopic values.

2.4 Characterization of groundwater in terms of sources, origin, and the main recharge.

Hydrogeochemical studies are considered one of the most important tools to identify and control the interaction processes of groundwater with aquifer minerals (Saber *et al.,* 2019). Several interaction processes are accountable for groundwater chemistry, such as soil-rock water interaction during groundwater flow and recharge, extended aquifer storage, and mineral species dissolution. The complexity of the hydrogeochemistry of the aquifers can be

understood through understanding the geochemical process, major ionic chemistry, and local geology. Hence, the major geochemical processes within basement aquifers are ionic exchange, evaporation, and dissolution of carbonates, gypsum, and silicates (Postma *et al*., 2008).

The evaporation process is shown by temporal variation in the saturation index of minerals and the ion-exchange process taking place when there is a concentration of ions such as calcium, magnesium, and sodium (Elango and Kannan, 2007). Major natural factors governing the formation of groundwater chemistry are rock dominance and the dissolution or precipitation of minerals, as well as cation exchange. However, the inputs of shallow groundwater evaporation and human activities are well explained in some cases due to the presence of stable isotopes and the occurrence of nitrates (Khogali *et al*., 2020).

Salinization is the main source that modifies the quality of groundwater and can be identified through exploratory hydrogeochemical and isotopic methods (Luo *et al*., 2018). Hence, the mineralogical composition of the rocks within the aquifers can be reflected in the isotopic and chemical composition of the groundwater. Such a system can then detect localized recharge areas and determine the origin of groundwater as well as individual chemical components (Postma et al., 2008). The composition of groundwater can also give information on the processes of water-rock interaction and microbial processes within the aquifers. A combination of dissolved cations and anions in solutions is a result of chemical weathering happening in different parent rocks within the aquifers, such as carbonates, silicates, and evaporites (Khogali *et al*., 2020).

2.5 Groundwater Recharge

Groundwater recharge is generally defined as water that moves from the land surface or unsaturated zone into the saturated zone, forming an addition to the groundwater reservoir (de Vries and Simmers, 2002; Scanlon et al., 2002; Nimmo et al., 2005). Sources of recharge include natural phenomena like precipitation, lakes, ponds, and rivers and human-induced phenomena like artificial recharge, irrigation, leaking water mains, septic tanks, sewers, gardens, and other public facilities. Surface water bodies, for example, rivers and lakes, do not always act as recharge sources. Instead, they can act as aquifer discharge points as well.

Groundwater recharge is an important process of the hydrological cycle that replenishes groundwater. Understanding the dominant groundwater recharge mechanisms therefore helps water resource managers understand if groundwater is being renewed annually or not. It also

helps in the identification of the potential vulnerability of the resource to climatic variations and further understanding if groundwater is also vulnerable to anthropogenic contamination.

CHAPTER THREE: MATERIALS AND METHODS

3.1 Description of the study area

The study was carried out in Traditional Authority Mwaulambya and Mwenemisuku in Chitipa district in northern Malawi. The district has a total area of 4,288 square kilometers with a population of 228,732 people (National Statistics, 2018).

3.1.1 Location

Chitipa district lies between latitudes 9° 42' 8" S and; between longitudes 33° 16' 10" E (Figure 1). It is bordered by two international boundaries that is Tanzania to the North (Ileje district) and Zambia to the west (Isoka district). It locally shares boundaries with Karonga to the North East and Rumphi district to the South. The district lies at a distance of 329 km from Mzuzu, the northern region's commercial city, and 691 km away from Lilongwe, the Capital City of Malawi. Figure 1, shows a map of Chitipa district and the twenty-five sampled boreholes.

3.1.2 Weather and Climate

Chitipa district has a tropical climate, with two main distinctive seasons: wet and dry seasons. The wet season starts in November and ends in May, while the dry season lasts from May through October. Some parts of the district such as Misuku Hills receive rains up to June (Chitipa SEP, 2017). The average annual temperature for the district is 20°C, with an average monthly temperature range of 6.1 °C. The total annual precipitation is 987.8 mm (Chitipa SEP, 2017).

3.1.3 Geology

Chitipa district is mainly underlain by metamorphic and igneous rocks of the pre-Karroo Malawi basement complex (Chitipa SEP, 2017). The district is underlain by igneous rocks of the following types: syenite, sodalite-syenite, nepheline-syenite, pyroxenite, carbonatite, and pegmatite (Chitipa SEP, 2017). Metamorphic rocks like gneiss and IIIAB iron meteorite are present in the district. Sedimentary complexes are also located in the basement complex, especially in North Rukuru and Nthalire. Alluvial and residual sediments dominate the Kaseye area.

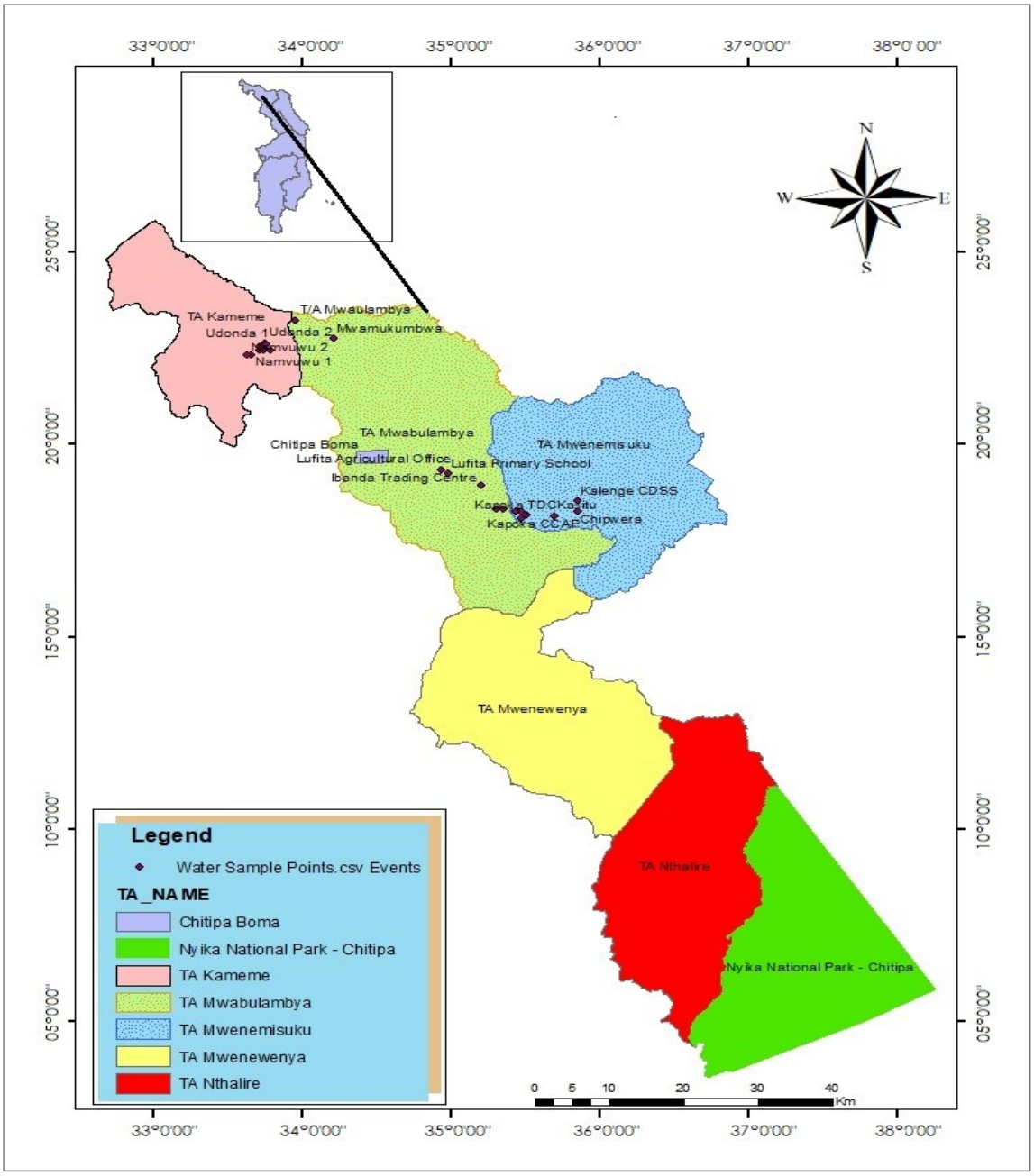


Figure 1: Map of Chitipa district showing the study area, TA Mwaulambya and Misuku.

3.1.4 Hydrological setting and water resources

Geological terrain defines the structure and aquifer units in Malawi. These are the rift valley areas overlain by thick alluvium, the plateau area composed of weathered material, and the mountain area exposing basement rocks (GOM, 2017). Aquifer structure and units on a macroscale are divided into three aquifers: the quaternary alluvium, the weathered basement, and the fractured basement rock. Quaternary aquifers are commonly found in the lowland areas

in the vicinity of Lake Malawi and Shire River Valley, weathered and fractured aquifers in highlands and plains (Council Geoscience, 2018).

Among the three aquifers, the weathered and the alluvium aquifers are of moderate to high yield and development (MOG, 2007). These two aquifers can be considered permeable layers, according to Darcy's theory. On the other hand, the basement rock is regarded as an impermeable aquifer, and runoff on the surface follows the porosity, infiltration, and seepage paths (Woessner and Poeter, 2020). Chitipa district depends on boreholes, gravity-fed schemes, taps, and protected wells as sources of water, and this applies to all five traditional authorities.

3.2 Research Design

This study employed a quantitative research design (QRD). The QRD was used because it produces objective data that can be communicated through numbers and statistics. It also provides a systematic approach to investigating a hypothesis and provides room for replication of the study by other researchers.

3.3 Data collection

3.3.1 Water sample collection

Groundwater samples were collected from 25 randomly selected boreholes in the two TAs of Mwaulambya and Misuku in Chitipa district. Groundwater sampling was provided. geographical spread and balanced hydrogeological coverage of the basement and superficial aquifer systems. Boreholes from different villages in the areas were selected to ensure maximum coverage of each TA. The water samples were collected in both the dry and rainy seasons. Water samples for anion and cation analysis were collected using 500 mL high-density polyethylene (HDPE) sampling bottles. Before sample collection, the bottles were cleaned using a non-phosphate detergent and rinsed three times with deionized water (DI).

Two sets of triplicate samples were collected at each water point. One set was for anion analysis and the other for cations between October 2021 and April 2022; a replicate sample was also collected for isotope analysis, yielding a total of 275 samples (50 stable isotope samples and 225 hydrogeochemical samples). The water samples for anions were collected and transported in cooler boxes to the lab, where they were stored at 4°C in between analyses. For cation preservation, 3 ml of 10% (V/V) nitric acid solution was added to the water to ensure that cations do not precipitate or adsorb to the surface of the containers (CCME, 2012).

Samples for environmental stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) determination were collected using 15 ml dedicated amber bottles, and samples were filtered using filter membranes with pore sizes of 0.45 µm. The sampling bottles were airtight-filled. Samples were stored at 4°C and away from sunlight during transportation and holding at the laboratory (Banda *et al*., 2020). A single bottle of analyte water was collected per sampling point in each season.

3.3.2 Water sample analysis

3.3.2.1 Determination of temperature, pH, EC, and TDS

Levels of temperature, pH, EC, and TDS were determined on site using a pH-EC-TDS multimeter (Model HI98129, Hanna Technologies Ltd., USA). After the collection of the unacidified sample, the levels of temperature, pH, EC, and TDS were immediately measured in the sample from the sampling bottles.

3.3.2.2 Determination of carbonate, bicarbonate, and chloride

Concentrations of carbonate and bicarbonate were determined titrimetrically according to standard procedure (APHA, 2017) at UNILIA. A 50-mL water sample was pipetted into a 250-mL conical flask. Four drops of phenolphthalein indicator solution were then added to the water sample. When a pink color was produced, the sample was titrated against 0.02 N sulfuric acid until the color was discharged. The volume of titrant used was then recorded as P. A drop of methyl red indicator was then added to the titration mixture, and the titration was continued until a light pink color was obtained. The total volume of the titrant was recorded as T.

Carbonate, mgL^{-1} was computed according to Equation 1:

$$CO_3^{-2}\left(\frac{mg}{L}\right) = \frac{2*P*N*30000}{50\ mL} \qquad \text{Equation 1}$$

Bicarbonate, mgL^{-1} was computed according to Equation 2:

$$HCO_3^{-}\left(\frac{mg}{L}\right) = \frac{(T-2P)*N*61000}{50\ mL} \qquad \text{Equation 2}$$

where N = normality of H_2SO_4.

Levels of Chloride were determined by the Mohr method (APHA, 2017). A 100 mL water sample was pipetted into a 250 mL conical flask. Using a measuring cylinder 1 mL potassium chromate indicator solution was then added to the water sample. The water sample was then titrated with 0.0141 N standard silver nitrate solution until a faint reddish-brown color persisted. The titer volume T was recorded. The reagent blank B was also determined by titrating 100 mL of the distilled water.

Chloride, mgL^{-1} was then computed per Equation 3:

$$Cl^{-}\left(\frac{mg}{L}\right) = \frac{(\mathrm{T} - \mathrm{B}) \times \mathrm{N} \times 35.540}{100\ mL} \qquad \text{Equation 3}$$

where N = Normality of $AgNO_3$, T = Titre volume for the sample, and B = Titre volume for the blank.

3.3.2.3 Determination of sodium and potassium

Levels of Na^{+} and K^{+} were determined using flame photometry (Model 410 Flame Photometer, Sherwood**,** UK). For each metal, a calibration curve was prepared automatically using 0.0, 1.0, and 10 mgL^{-1} standard solutions. The water samples were then aspirated into the photometer and the concentration of the metal in the water sample was read directly from the photometer at the appropriate wavelength. Sodium was measured at 589 nm. Potassium was measured at 285.2nm.

3.3.2.4 Determination of magnesium and calcium

Levels of Mg^{+2} and Ca^{+2} were determined using AAS (AA 500 Spectrophotometer, pg Instruments, UK). For each metal, a calibration curve was prepared automatically using 0.0, 1.0 and 5 mgL^{-1} standard solutions. The water samples were then aspirated into the AAS and the concentration of the metal in the water sample was read directly from the AAS at the appropriate wavelength. Magnesium was measured at 285.2 nm. Potassium was measured at 422.7 nm.

3.3.2.5 Determination of sulphate and nitrate

Levels of SO_4^{-2} and NO_3^{-} were determined using UV/VIS spectrophotometry (Model ASD, Malvern Panalytical, India). Sulphate was measured at 430 nm after precipitation as barium sulphate (APHA, 2017). A 50 mL acidified water sample is pipetted into a 300 mL conical

flask. Using a measuring cylinder 10 mL of sodium chloride hydrochloric acid solution (240 g NaCl+20 mL32 % HCl in 1000 mL solution) was added to the water sample. Barium chloride of quantity 0.5 g was then added to the sample mixture and stirred immediately for 1 minute. The absorbance of the sample, A was then read using a 10 mm size cell on the spectrophotometer at 430 nm. The spectrophotometer was set at zero using distilled water as a blank. Sulphate, mgL^{-1} is then computed using Equation 6:

$$SO_4^{-2}\left(\frac{mg}{L}\right) = \frac{A*1000}{50\ mL} \quad \text{Equation 4}$$

where A = Absorbance of the sample.

Concentration of Nitrate was determined using the salicylate method (APHA, 2017). A 5.00 mL water sample portion was pipetted into a 100 mL pyrsex beaker. This was noted as volume of sample v. Using a pipette, 2.0 mL of sodium salicylate solution (0.5 % w/v) was added to the sample. After thorough mixing the sample mixture was evaporated to dryness on a water bath. The beaker containing the sample residue was then removed from the water bath; 1.0 mL of concentrated sulphuric acid was then added to the sample residue. After 10 minutes 50 mL of distilled water was added to the beaker followed by 10 mL of sodium hydroxide (25 % w/v). After cooling the sample mixture was transferred to a 100 mL volumetric flask and made up to the mark. The absorbance of the absorbance was read at 410 nm. A standard calibration curve was prepared using 0.0, 0.5, 1.0, 1.5 and 2.0 mgL^{-1} nitrate solutions. The standard solutions suffered the same treatment as the samples and a graph of absorbance, y was plotted against standard concentration, c with the y-intercept set at 0. From Equation 5:

$$y = mc \quad \text{Equation 5}$$

Levels of Nitrate, mgL^{-1} were calculated per Equation 6:

$$NO_3^-\left(\frac{mg}{L}\right) = \frac{a}{m} \quad \text{Equation 6}$$

where a = absorbance of the sample and m is slope of the calibration curve.

3.3.2.6 Water isotope analysis

Levels of water stable isotopes, deuterium (δ^2H) and oxygen-18 ($\delta^{18}O$) ratios, were determined using an automated cavity ring-down spectroscope, Picarro Laser Water isotopic Analyser at the Central Water Laboratory. The water laser spectroscopy-based method approach was used

in the analysis. The analysis involved daily calibration of heavy and light standards to include the anticipated range of isotopic composition in samples, alongside use of a daily control mid-range standard intermediate between heavy and light standards. The quality of measurement was checked through inspection of concentration peaks with an acceptable range of 19,000 – 21,000 ppm. The isotopic analysis was conducted in line with International Standard Procedures (Banda *et al*., 2020).

3.4 Data Analysis

3.4.1 Hydrogeochemistry

Data entry and analysis were carried out using IBM Statistical Package for Social Sciences version 20 (SPSS, Michigan Avenue, Chicago, IL, USA). The student's t-test was used to determine whether there were statistically significant variations between levels of parameters in dry and wet seasons at a 95% confidence level. A Spearman's rank correlation was run to establish the relationship between water quality parameters with season and source.

3.4.2 Quality control and assurance of results and analysis

Charge balance error € on each sample was used for quality control and assurance of hydrochemical data. The charge balance error, E was obtained using Equation 7:

$$\text{Charge balance error } = \left(\frac{\Sigma mc - \Sigma ma}{\Sigma mc + \Sigma ma}\right) \times 100\ \% \qquad \text{Equation 7}$$

where m_c is the milligram equivalent of cations and m_a is the milligram equivalent of anions was used to check the accuracy of the data. A value of € less than 5 percent indicates accurate data. The 5% charge balance was chosen over 10% because it produces more credible results.

3.4.3 Determination of levels of environmental water-stable isotopes (δ18O and δ2H) from different water sources.

The isotopic ratios ($\delta^{18}O$) and $\delta^{2}H$) given in d **-** units were calculated concerning the standard sample using Equation 8:

$$d_{sample} = \left[\left(\frac{R_{sample}}{R_{sample}}\right) - 1\right] \times 1000\left(\frac{0}{100}\right) \qquad \text{Equation 8}$$

In which R_{sample} and $R_{standard}$ represent the ratio of heavy to light isotopes in the sample and standard respectively used to determine the origin(s) of the water. A plot of $\delta^{2}H$ vs. $\delta^{18}O$ along the Global Meteoric Water Line on a graph indicates atmospheric precipitation as the recharge

source of the groundwater. The Local Meteoritic Line is not available for Malawi hence the choice of the GMWL.

3.4.4 Hydrogeochemical processes

A Gibbs plot i.e., the plot of TDS versus $Na/Na^{+} + Ca^{+2}$and TDS vs. $Cl/Cl^{-}+HCO_3^{-}$ was used to determine major processes controlling the groundwater chemistry (atmospheric precipitation, rock weathering, and evaporation)**.** Zones on the plots are indicative of the hydrochemical processes involved. Piper diagrams were used to show the clustering of samples and inter-hydrochemical facies of samples or clusters of samples in the TAs under study.

3.5 Study Limitations

The major limitations of the study were:

i. Impassable roads during the rainy season. Borehole visits were postponed until the rains subsided. However, the sampling was done within the stipulated time frame.

ii. Multiple chemical suppliers had to be involved in the provision of chemicals to ensure a standard supply at a reasonable rate. However, we negotiated a fixed-term contract with a reliable supplier to secure standard suppliers and potentially a better rate.

iii. This study only used a single season (wet and dry) to understand the variations. This, to an extent, might have led to some variations in results considering changes in weather within short periods within the area.

Table 1: Methodology Matrix

Specific Objective	Data to be collected	Methods of Data collection	Data analysis	Analysis tool
To characterize the hydrogeochemical-stable isotopic composition (δ^2H and $\delta^{18}O$) of groundwater in Chitipa district.	▪ Isotopic ratios of O - 18 and H - 2	▪ Piccaro Laser Water Isotopic analyzer	▪ Isotopic plots of δ^2H against $\delta^{18}O$ along GMWL	▪ Microsoft Excel
To assess changes in the hydrogeochemical and isotopic composition of groundwater with seasons in Chitipa district.	▪ Physical water parameters; pH and TDS ▪ Anions concentrations ▪ Cations concentrations	▪ In situ Analysis using a pH – EC – TDS – Temperature multimeter ▪ Titrimetric and Spectrophotometry for anions. ▪ Flame photometry for K and Na ▪ AAS for Ca and Mg	▪ Descriptive statistics ▪ Student's t-test	▪ SPSS
To determine groundwater recharge sources such as precipitation, and infiltration in Chitipa district.	▪ Anions concentrations ▪ Cations concentrations	▪ Titrimetry and Spectrophotometry for anions. ▪ Flame photometry for K and Na ▪ AAS for Ca and Mg	Piper diagrams	▪ AquaChem software
To examine the hydrogeochemical processes that govern groundwater quality in the Chitipa district.	▪ TDS ▪ Sodium and calcium ion concentrations ▪ Chloride and bicarbonate ion concentrations	▪ As above	▪ Gibbs plot	▪ AquaChem software

CHAPTER FOUR: RESULTS

4.0 Introduction

This chapter presents the findings of this research.

4.1. Hydrogeochemical Composition

The hydrogeochemical characteristics of the groundwater studied included physical and chemical properties of the groundwater. Details of the hydrogeochemical parameters are presented in the subsequent subsections.

4.1.1 Physical parameters of groundwater in the study area

This section presents the physical parameters of the groundwater samples collected during both the dry and wet seasons. These parameters include electrical conductivity (EC), pH, total dissolved solids (TDS), and temperature. The levels of electrical conductivity (EC), varied significantly between the dry and wet seasons, $p < 0.05$ (**Table 5**). During the dry season, EC levels ranged from 202 to 263 *u*S/cm (Figure 2), indicating relatively low conductivity. In the wet season, the EC levels showed greater variation between boreholes, ranging from 4.7 to 1363 *u*S/cm (Figure 2). The average EC for the wet season was 308 *u*S/cm, higher than the average for the dry season, 236. *u*S/cm. The EC was positively correlated with TDS, $R^2 = 1$.

From **Table 2** it can be seen that: pH levels in the dry season ranged from 6.5 to 7.3, with an average value of 6.8. On the other hand, in the wet season, pH levels varied from 6.2 to 7.5 (Table 2), with an average of 6.8. These pH values indicate slightly acidic to neutral water in both seasons. However, it's worth noting that the pH levels did not show significant variations between the seasons (**Table 2**).

Total dissolved solids (TDS), which measure the concentration of inorganic salts and minerals in water, also exhibited distinct variations. During the wet season, TDS levels ranged from 2.82 to 636 ppm (Table 2). In comparison, the dry season recorded lower TDS levels, ranging from 132.6 to 217.8 ppm (**Table 2**).

Lastly, the temperature of the water samples fluctuated between the dry and wet seasons. In the dry season, temperatures ranged from 24.3 to 30.0 °C, while during the wet season, they ranged from 21.3 to 25.9 °C. These temperature ranges are within the typical ambient temperature for the area under observation.

Overall, these results indicate that groundwater composition varied significantly between the dry and wet seasons in terms of EC, TDS, and temperature. The EC and TDS levels did not show a general trend of increase or decrease between seasons. For temperature, there was wider variation during the dry season compared to the wet season, and the general trend was that the dry season registered higher temperature levels than the wet season.

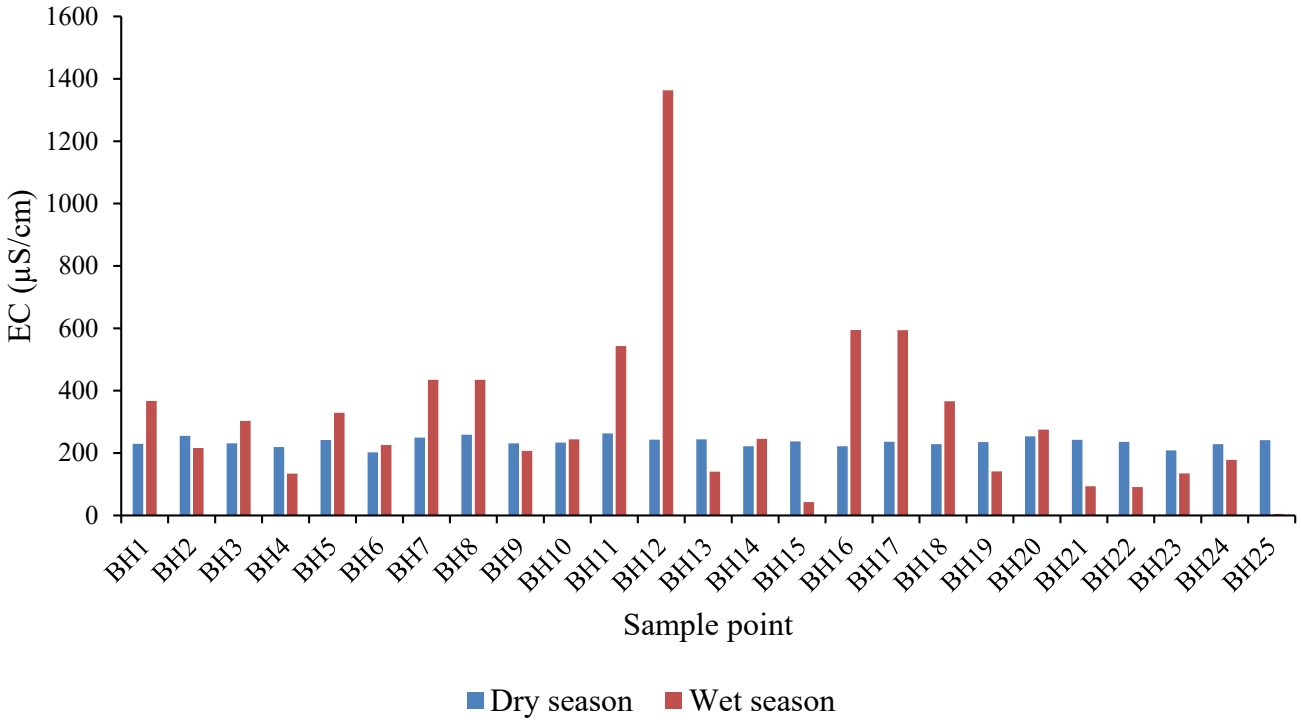


Figure 2: EC levels for each borehole during the dry and wet seaso

Table 2: Mean levels of water quality physical parameters for the two seasons in the study area

BH NO.	Temperature		pH		EC μS/cm		TDS mgL^{-1}	
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
BH1	27.2 ± 0.4	25.9 ± 0.1	6.5 ± 0.4	6.4 ± 0.1	229.6 ± 0.6	367 ± 2	132.3 ± 0.6	173 ± 0
BH2	26.3 ± 0.6	24.9 ± 2.7	6.8 ± 0.4	6.5 ± 0.0	255.1 ± 0.2	216 ± 2	261.7 ± 2.1	101.7 ± 0.6
BH3	25.4 ± 0.6	24.1 ± 0.2	7.5 ± 0.4	6.2 ± 0.0	231.1 ± 1.1	303 ± 1	113.3 ± 0.6	142.7 ± 0.6
BH4	26.7 ± 0.1	24.9 ± 4.4	7.0 ± 0	6.3 ± 0.1	219.2 ± 0.8	134 ± 0	107 ± 1	63 ± 0
BH5	25.2 ± 0.1	24.2 ± 0	6.7 ± 0.1	6.4 ± 0.1	241.9 ± 0.2	329 ± 2	143 ± 1	154.7 ± 1.5
BH6	25.5 ± 0.2	24.5 ± 0.1	6.8 ± 0.4	6.3 ± 0.1	202.3 ± 1.2	226 ± 2.3	89.7 ± 0.6	107 ± 1
BH7	24.8 ± 0.1	21.8 ± 0.2	6.6 ± 0.4	7.2 ± 0.3	249.6 ± 0.6	434.7 ± 1.2	170.3 ± 2.1	204.7 ± 0.6
BH8	25.3 ± 0.3	21.7 ± 0.1	6.7 ± 0.3	6.8 ± 0.4	258.7 ± 2.3	434.7 ± 1.2	91.7 ± 0.6	204.7 ± 0.6
BH9	26 ± 0.1	24.8 ± 0.1	6.5 ± 0.0	7.2 ± 0.4	230.9 ± 0.5	206.7 ± 1.2	127.7 ± 0.6	98 ± 1
BH10	27.2 ± 0.3	24.3 ± 0.1	7 ± 3	7.1 ± 0.2	233.8 ± 4.1	243.7 ± 0.6	107.3 ± 0.6	113.3 ± 0.6
BH11	26.3 ± 0.2	21.9 ± 0	6.8 ± 0.1	7.1 ± 0.3	263 ± 2	543 ± 1	411.3 ± 1.2	254 ± 2
BH12	25.3 ± 0.4	21.8 ± 0.1	7.3 ± 0.3	6.9 ± 0.2	242.8 ± 1.6	1363.3 ± 5.7	616.7 ± 4.0	636.3 ± 1.5
BH13	28.3 ± 1.7	21.8 ± 0.1	7.3 ± 0.4	6.7 ± 0.3	243.9 ± 4.9	140 ± 0	139.7 ± 0.6	66.3 ± 0.6

BH14	25.7 ± 1.1	21.7 ± 0.1	7.0 ± 0.1	7.1 ± 0.2	222 ± 0.3	245.3 ± 1.2	65 ± 1.2	115.3 ± 0.6
BH15	27.2 ± 2.1	21.3 ± 0.1	6.7 ± 0.3	6.7 ± 0.4	237.3 ± 3.6	42.7 ± 1.2	127 ± 1.7	19.3 ± 0.6
BH16	28.5 ± 1.4	24.3 ± 0.2	6.8 ±0.4	7.5 ± 0.1	221.8 ± 3.2	594.3 ± 2.3	42.7 ± 0.6	278.3 ± 2.1
BH17	30 ± 0.2	24.3 ± 0.2	6.6 ± 0.5	6.5 ± 0.6	236 ± 10.8	594 ± 2	37.7 ± 0.6	343 ± 5
BH18	26.1 ± 0.3	21.8 ± 0.2	6.6 ± 0.3	7.1 ± 0.2	228.6 ± 5.7	366 ± 3	45.7 ± 0.6	172.7 ± 1.5
BH19	26.8 ± 1.2	21.9 ± 0.1	6.5 ± 0.3	7 ± 0.3	235.1 ± 5.5	141 ± 1.2	85 ± 0.6	67.3 ± 0.6
BH20	26.9 ± 0.2	21.7 ± 0.2	6.5 ± 0.3	6.8 ± 0.4	253.6 ± 2.3	275 ± 1.2	53 ± 1.2	129.6 ± 0.6
BH21	28.7 ± 1.7	21.6 ± 0.6	6.8 ± 0.4	6.8 ± 0.2	242.2 ± 1.8	93.6 ± 1.2	136 ± 1	44.3 ± 0.6
BH22	29.9 ± 0.1	21.4 ± 0.2	6.6 ± 0.5	6.8 ± 0.1	235.8 ± 10.4	91 ± 0	130.7 ± 0.6	43 ± 0
BH23	24.3 ± 0.4	22.4 ± 0.2	6.7 ± 0.2	7.2 ± 0.2	208.6 ± 3.9	134.7 ± 1.2	225.3 ± 2.5	63.7 ± 0.6
BH24	25.8 ± 0.7	21.8 ± 0.2	6.9 ± 0.2	6.7 ± 0.2	228.4 ± 1.9	178 ± 0	297.3 ± 3.1	83.3 ± 1.2
BH25	29.2 ± 0.4	21.7 ± 0.2	6.9 ± 0.2	6.2 ± 0.3	241.2 ± 0.4	4.7 ± 0.6	173.3 ± 1.5	2.3 ± 1.2
WHO STDs	NA		6.5 – 8.5		-		3500	
MBS STDs	NA		6.5 – 8.5		1000		200	

4.1.2 Chemical Results

The chemical analysis categorized the studied parameters into cations and anions. Cations included potassium, calcium, magnesium, and sodium, while anions encompassed chloride, nitrate, sulphate, and bicarbonate. The concentrations of some cations and anions are presented in: **Table 4** (sodium, magnesium, carbonate, and sulphate); **Figure 3** (potassium), **Figure 4** (calcium), **Figure 5** (bicarbonate), **Figure 6** (chloride) and **Figure 7** (nitrate).

4.1.2.1 Cations

From **Figure 3** it can be seen that; during the dry season, potassium concentrations ranged from 1.45 to 5.8 mgL^{-1}, with an average mean of 4.01 mgL^{-1}. Potassium levels during the wet season varied between 3.1 and 7.8 mgL^{-1}, with an average of 4.9 mgL^{-1}. Calcium concentrations during the dry season ranged from 7.9 to 12.8 mgL^{-1} (Figure 4), with an average mean of 9.7 mgL^{-1}. In the wet season, the range was between 6.2 and 13.9 mgL^{-1} (Figure 4), with an average concentration of 8.4 mgL^{-1}. Magnesium concentrations during the dry season were found to vary between 2.42 and 62.8 mgL^{-1} while in the wet season, the levels ranged from 2.2 to 59.9 mgL^{-1} (Table 2). The mean levels for magnesium were 10.8 and 10.5 mgL^{-1} during the dry and wet seasons respectively. Also, from **Table 2**, sodium concentrations during the dry season ranged from 10 to 59 mgL^{-1}, with an average of 24.9 mgL^{-1}. In the wet season, sodium concentrations ranged from 11 to 69 mgL^{-1}, with an average of 26.6 mgL^{-1}.

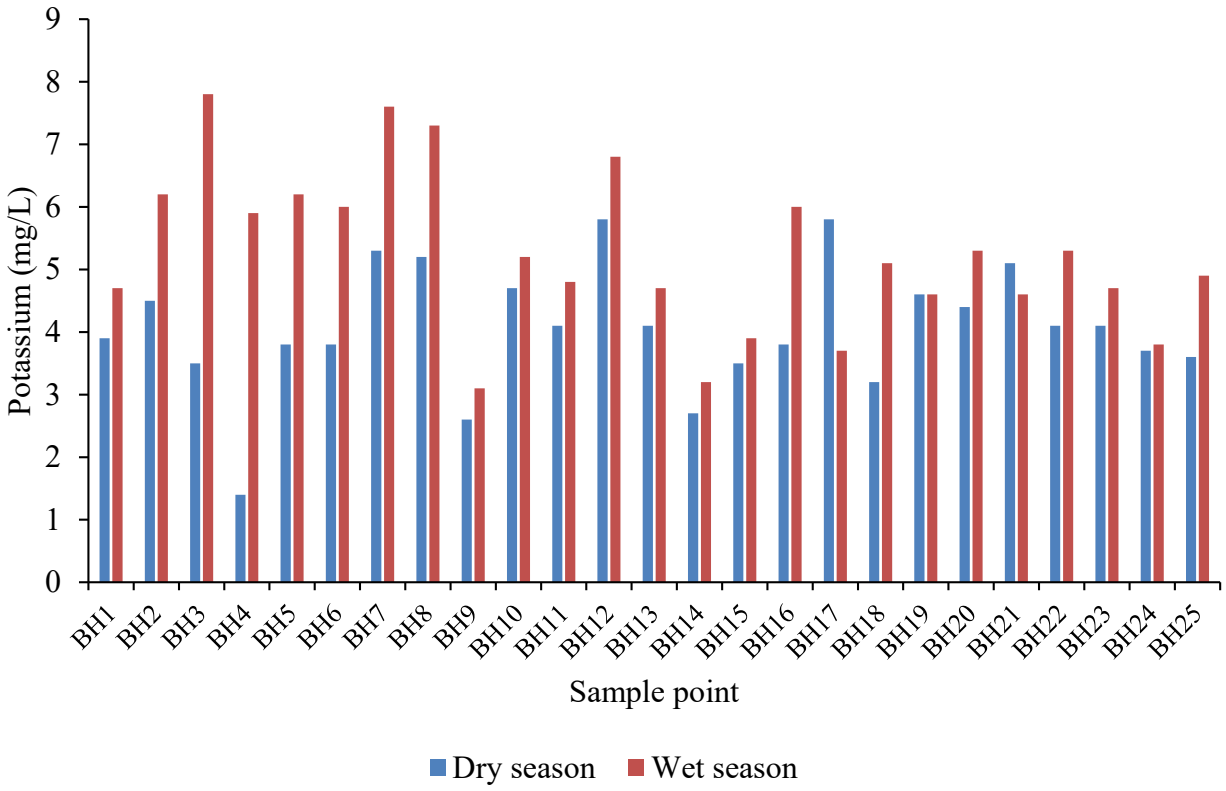


Figure 3: Potassium levels at each borehole during the dry and wet seasons

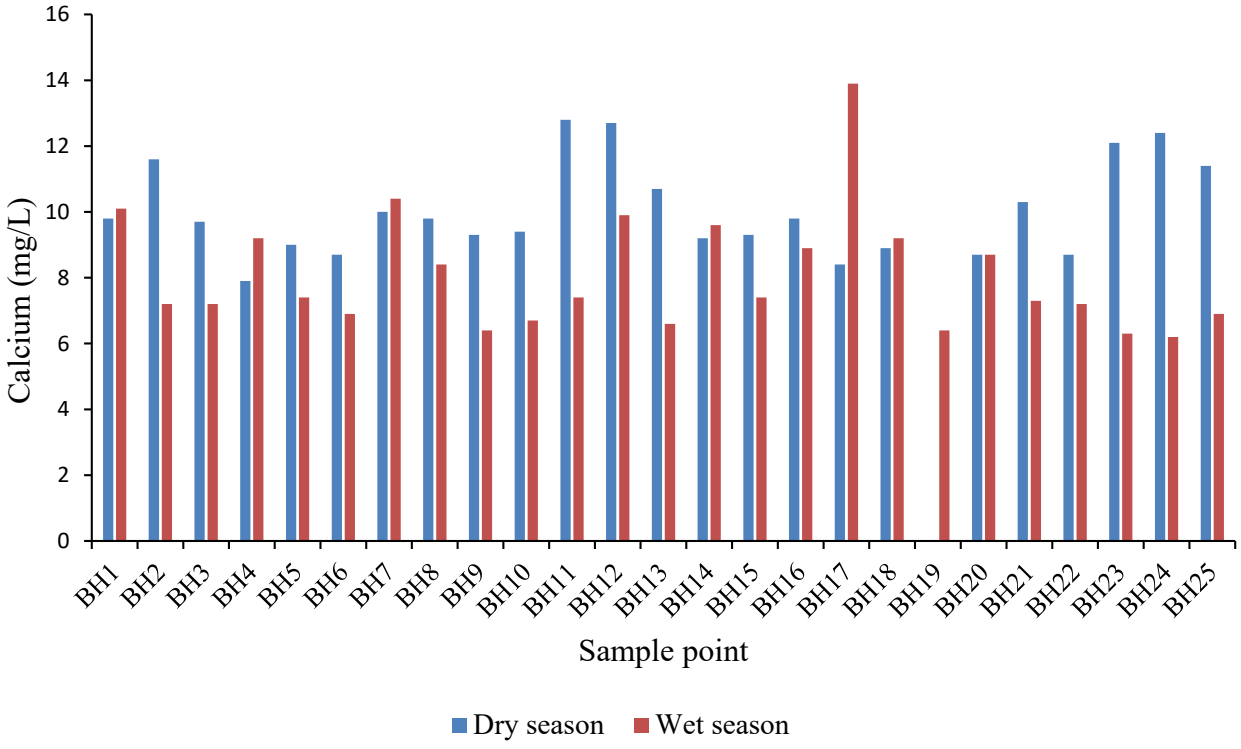


Figure 4: Calcium levels at each borehole during the dry and wet seasons

Table 3: Mean concentrations of cations and anions determined at the 25 boreholes during the dry and wet seasons in the study area

BH No	$Na^{+}mgL^{-1}$		$Mg^{2+}mgL^{-1}$		SO_4^{2-} MgL^{-1}	
	Dry	**Wet**	**Dry**	**Wet**	**Dry**	**Wet**
BH1	23 ± 3	21 ± 2	9.4 ± 0.3	10.7 ± 0.4	9.8 ± 0.6	10.1 ± 1.0
BH2	45 ± 2	58 ± 4	15.1 ± 0.5	14.5 ± 0.6	11.6 ± 0.2	7.2 ± 0.1
BH3	17 ± 1	16 ± 1	8.2 ± 0.3	9.4 ± 0.3	9.7 ± 0.2	7.2 ± 0.5
BH4	31 ± 4	30 ± 1	9.3 ± 0.2	9.2 ± 0.2	7.9 ± 0.8	9.2 ± 2.5
BH5	23 ± 2	23 ± 2	9.9 ± 0.4	9.9 ± 0.4	9.0 ± 0.1	7.4 ± 0.5
BH6	16 ± 2	15 ± 1	7.4 ± 0.3	7.1 ± 0.3	8.7 ± 0.2	6.9 ± 0.2
BH7	33 ± 3	33 ± 2	5.5 ± 0.1	5.1 ± 0.2	10.0 ± 0.2	10.4 ± 2.1
BH8	18 ± 2	20 ± 1	6.5 ± 0.2	6.5 ± 0.1	9.8 ± 0.5	8.4 ± 3.1
BH9	20 ± 3	19 ± 3	7.3± 0.2	7.2 ± 0.2	9.3 ± 0.8	6.4 ± 0.3
BH10	22 ± 1	23 ± 2	4.6 ± 0.3	4.2 ± 0.1	9.4 ± 0.3	6.7 ± 0.5
BH11	59 ± 3	69 ± 4	38.5 ± 0.1	36.1 ± 2.1	12.8 ± 0.6	7.4 ± 0.6
BH12	28 ± 2	26 ± 1	62.3 ± 1.0	59.9 ± 1.3	12.7 ±0.4	9.9 ± 0.8
BH13	32 ± 1	32 ± 3	7.9 ± 0.2	7.5 ± 0.3	10.7 ± 1.2	6.6 ± 1.0
BH14	15 ± 1	15 ± 2	5.2 ± 0.1	4.9 ± 0.5	9.2 ± 0.9	9.6 ± 3.1
BH15	19 ± 1	17 ± 1	8.6 ± 0.3	7.8 ± 0.4	9.3 ± 0.2	7.4 ± 1.4
BH16	16 ± 1	15 ± 2	2.4 ± 0.1	2.6 ± 0.1	9.8 ± 1.5	8.9 ± 0.3
BH17	13 ± 3	14 ± 2	2.6 ± 0.1	2.0 ± 0.2	8.4 ± 0.7	13.9 ± 5.3
BH18	13 ± 1	13 ± 2	3.2 ± 0.2	3.2 ± 0.1	8.9 ± 1.3	9.2 ± 1.1
BH19	18 ± 4	17 ± 3	6.2 ± 0.3	6.1 ± 0.2	9. 1 ± 0.4	6.4 ± 1.1
BH20	10 ± 2	11 ± 1	4.2 ± 0.4	4.2 ± 0.3	8.7 ± 0.5	8.7 ± 1.5
BH21	26 ± 1	25 ± 3	5.9 ± 0.2	5.6 ± 0.4	10.3 ± 0.1	7.3 ± 2.1
BH22	19 ± 1	19 ± 2	2.2 ± 0.1	2.4 ± 0.2	8.7 ± 2.5	7.2 ± 0.8
BH23	40 ± 5	59 ± 3	5.8 ± 0.2	5.2 ± 0.3	12.1 ± 0.9	6.3 ± 1.0
BH24	43 ± 3	62 ± 4	26.5 ± 1.0	26.5 ± 0.8	12.4 ± 0.8	6.2 ± 0.9
BH25	41 ±1	40 ± 2	5.6 ± 0.3	5.6 ± 0.4	11.4 ± 0.4	6.9 ± 1.5

4.1.2.2 Anions

The concentrations of anions in the boreholes during both the dry and wet seasons are shown in: Table 3 (sulphate); Figure 5 (bicarbonate); Figure 6 (chloride) and Figure 7 (nitrate). Bicarbonate levels ranged from 40.2 to 107 mgL^{-1} in the dry season (Figure 5), with an average of 62.5 mgL^{-1}. During the wet season, bicarbonate levels ranged from 73.1 to 193.9 mgL^{-1}, with an average of 115 mgL^{-1}. It is worth noting that TA Mwenemisuku consistently recorded the highest levels of bicarbonate in both seasons.

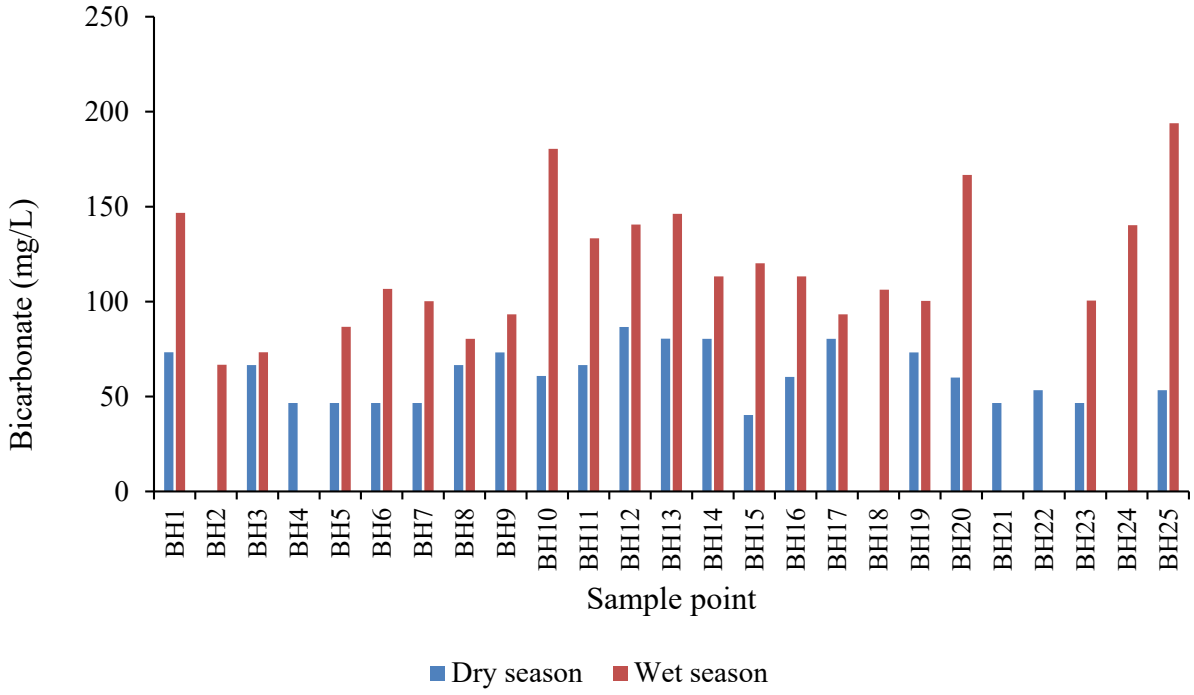


Figure 5: Levels of bicarbonate at each borehole during the dry and wet seasons.

Chloride ion concentration in the boreholes during the dry season varied from 1.8 to 38.2 mgL^{-1} – Figure 6, with an average of 10.5 mgL^{-1}. In the wet season, chloride concentrations ranged from 0.3 to 59 mgL^{-1}, with an average of 10.1 mgL^{-1}. Boreholes from TA Mwaulambya consistently had the highest chloride ion concentrations in both seasons.

Nitrate levels in the dry season ranged from 0.7 to 9.1 mgL^{-1}, with an average of 2.7 mgL^{-1}. In the wet season, nitrate levels varied from 0.3 to 68.6 mgL^{-1}, with an average range of 7.9 mgL^{-1}. TA Mwaulambya consistently had the highest nitrate levels in both seasons.

Sulphate concentration ranged from 3.1 to 40.3 mgL^{-1} (Table 2), with an average of 8.5 mgL^{-1}. Similar to the other anions, TA Mwaulambya had the highest concentration of sulphate in

both seasons. In the wet season, sulphate concentrations ranged from 3.1 to 39.6 mgL^{-1}, with an average of 8.1 mgL^{-}.

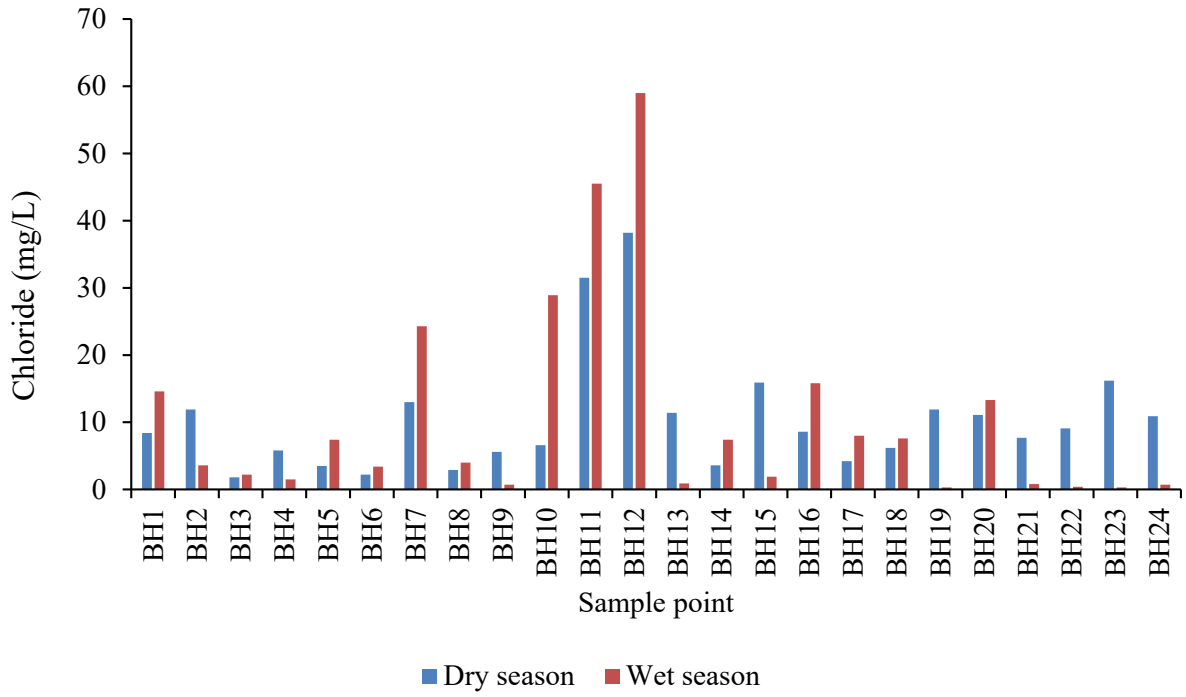


Figure 6: Levels of chloride at each borehole during the dry and wet seasons

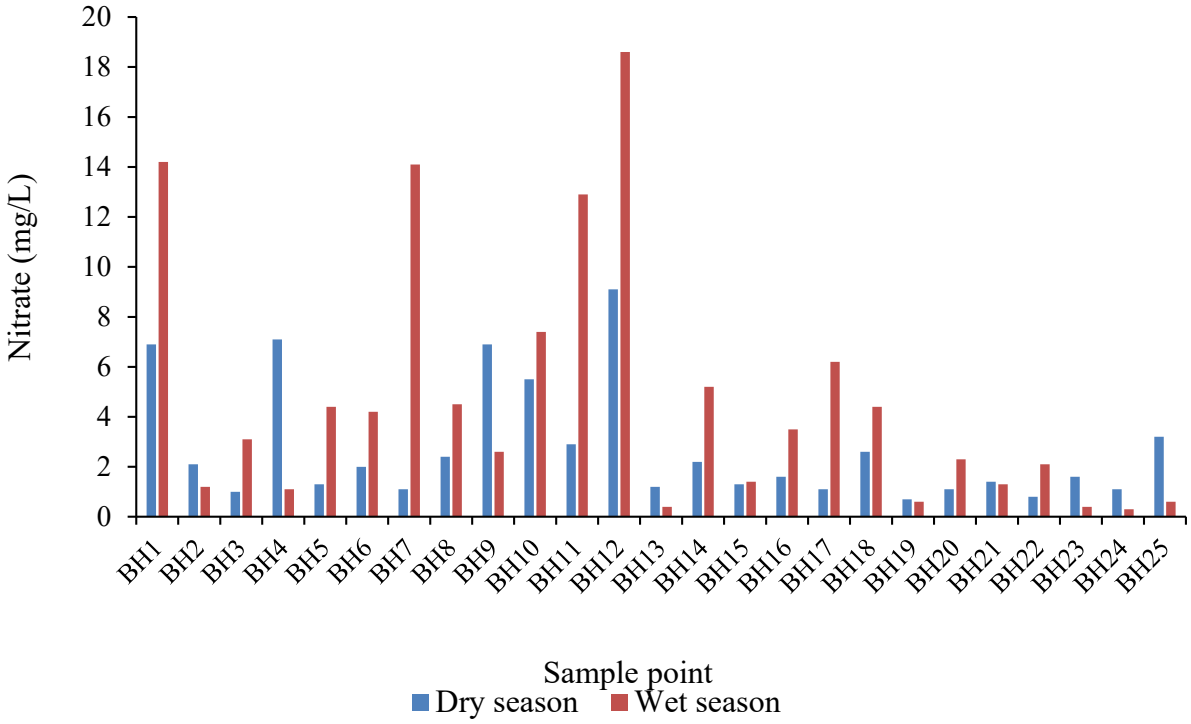


Figure 7: Levels of nitrate at each borehole during the dry and wet seasons

4.2 Ion Charge Balance Errors of Groundwater Quality

Table 4, presents the sum of anions and sum of cations in meq/L which were used to compute the ion charge balance (%) per Equation (E = (Σm c -Σm a/Σm c +Σm a)*100% also in the table. The charge balance was computed for each borehole in each season.

Table 4: Presents the sum of anions and the sum of cations in meq/L

BH NO	Dry season			Wet season		
	Σ Anions (meq/L)	Σ Cations (meq/L)	Charge balance (%)	Σ Anions (meq/L)	Σ Cations (meq/L)	Charge balance (%)
BH 1	2.13	2.37	-5.03	2.69	2.42	5.28
BH 2	3.54	3.89	-4.82	3.82	4.23	-5.14
BH 3	1.81	1.99	-4.633	1.85	2.03	-4.52
BH4	2.31	2.54	-4.88	2.43	2.67	-4.82
BH5	2.13	2.36	-5.05	2.13	2.34	-4.75
BH6	1.67	1.83	-4.82	1.87	1.74	3.79
BH7	2.25	2.52	-5.78	2.66	2.55	2.14
BH8	1.73	1.940	-5.65	2.23	2.01	5.18
BH9	1.78	2.00	-5.82	1.71	1.82	-3.11
B10	1.73	1.92	-5.26	2.02	1.81	5.46
BH11	5.84	6.48	-5.17	5.84	6.46	-5.03
BH12	6.33	7.12	-5.88	7.69	8.51	-5.05
BH13	2.42	2.68	-5.09	2.65	2.46	3.66
BH14	1.59	1.61	-0.56	1.65	1.51	6.63
BH15	1.91	2.09	-4.41	2.05	1.85	5.16
BH16	1.41	1.48	-2.37	1.62	1.46	5.06
BH17	1.49	1.35	4.99	1.65	1.56	2.67
BH18	1.50	1.36	5.09	1.57	1.42	5.22
BH19	1.70	1.87	-4.53	1.83	1.68	4.23
BH20	1.44	1.33	4.20	1.54	1.39	5.034
BH21	2.06	2.26	-4.75	1.90	2.03	-3.20
BH22	1.26	1.15	4.68	1.68	1.52	5.17
BH23	2.65	2.93	-4.89	3.13	3.43	-4.63
BH24	4.30	4.76	-5.16	4.77	5.28	-5.13
BH25	2.62	2.91	-5.10	2.95	2.67	4.92

4.3 Hydrogeochemical faces of groundwater

Identification of the hydrogeochemical faces of the groundwater was achieved by utilizing piper diagrams in Figures 8a and 8b, it is evident that the groundwater in the study area is mainly of mixed types, namely Ca-Na-HCO_3 and Ca-Mg-SO_4 (80 %). Further, the dominant cation was found to be Na^+, and the main anion present in the groundwater is bicarbonate (HCO_3^-). This was observed in all the 25 boreholes (100 %).

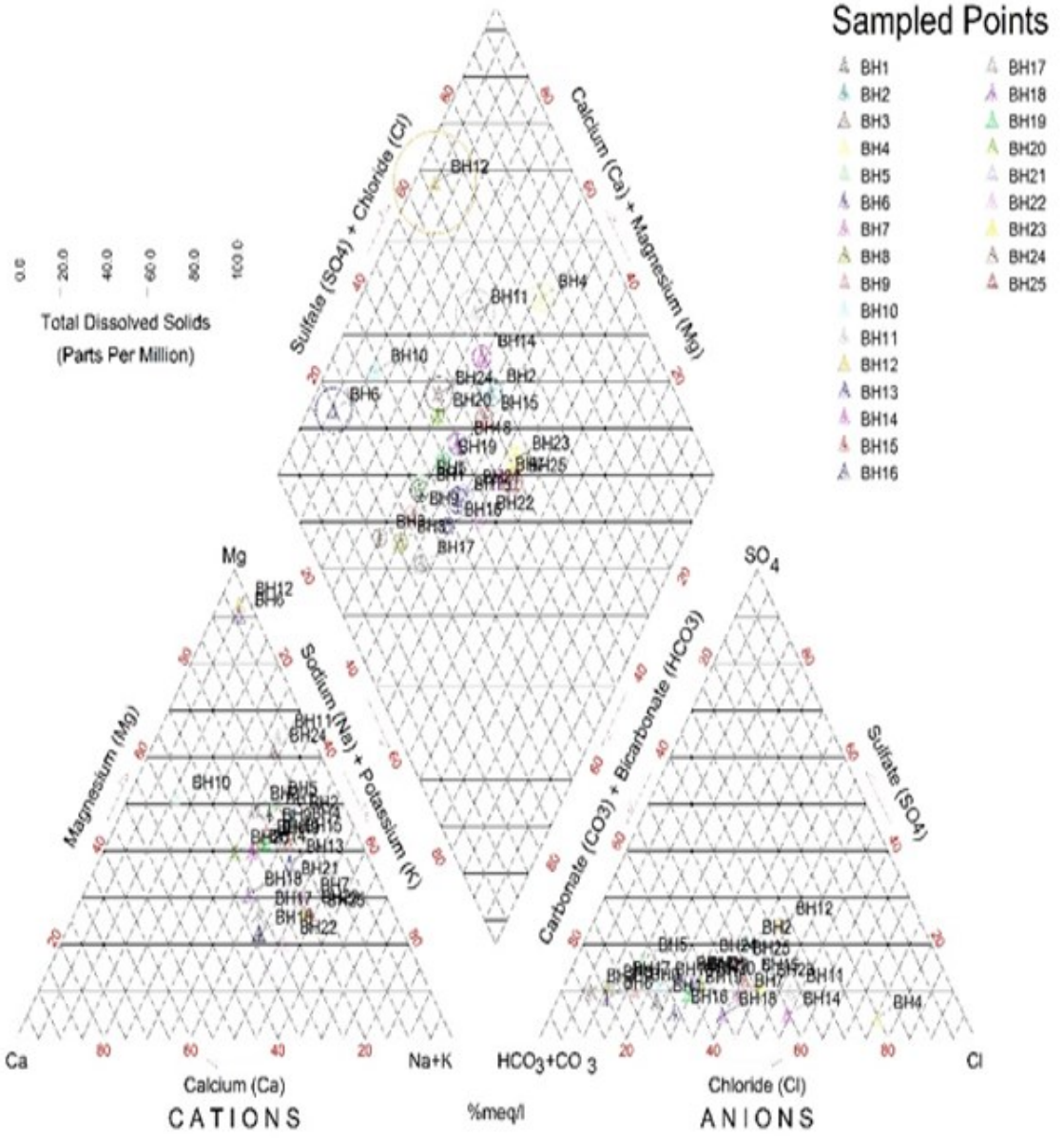
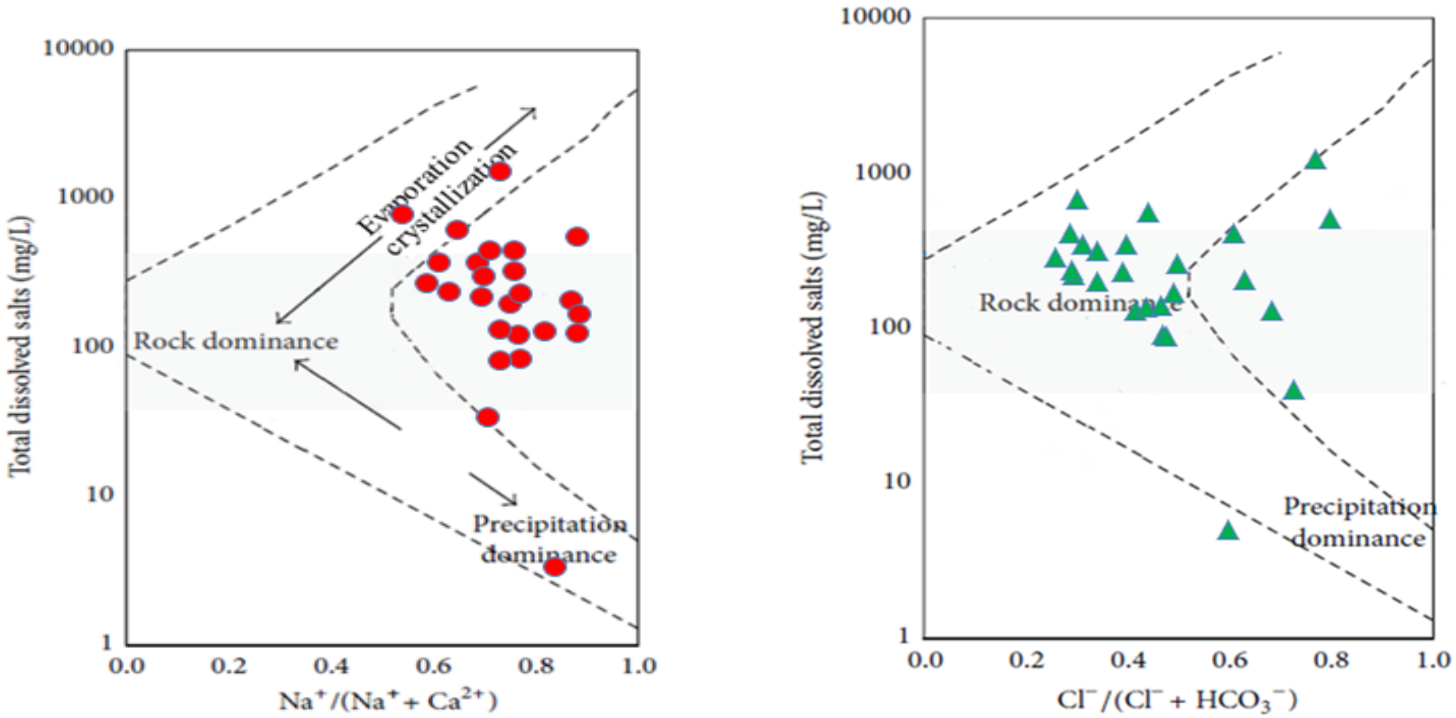


Figure 8(a): Piper diagram showing major hydrogeochemical facies of groundwater samples from Tas Mwaulambya and Misuku in Chitipa district in the wet Season

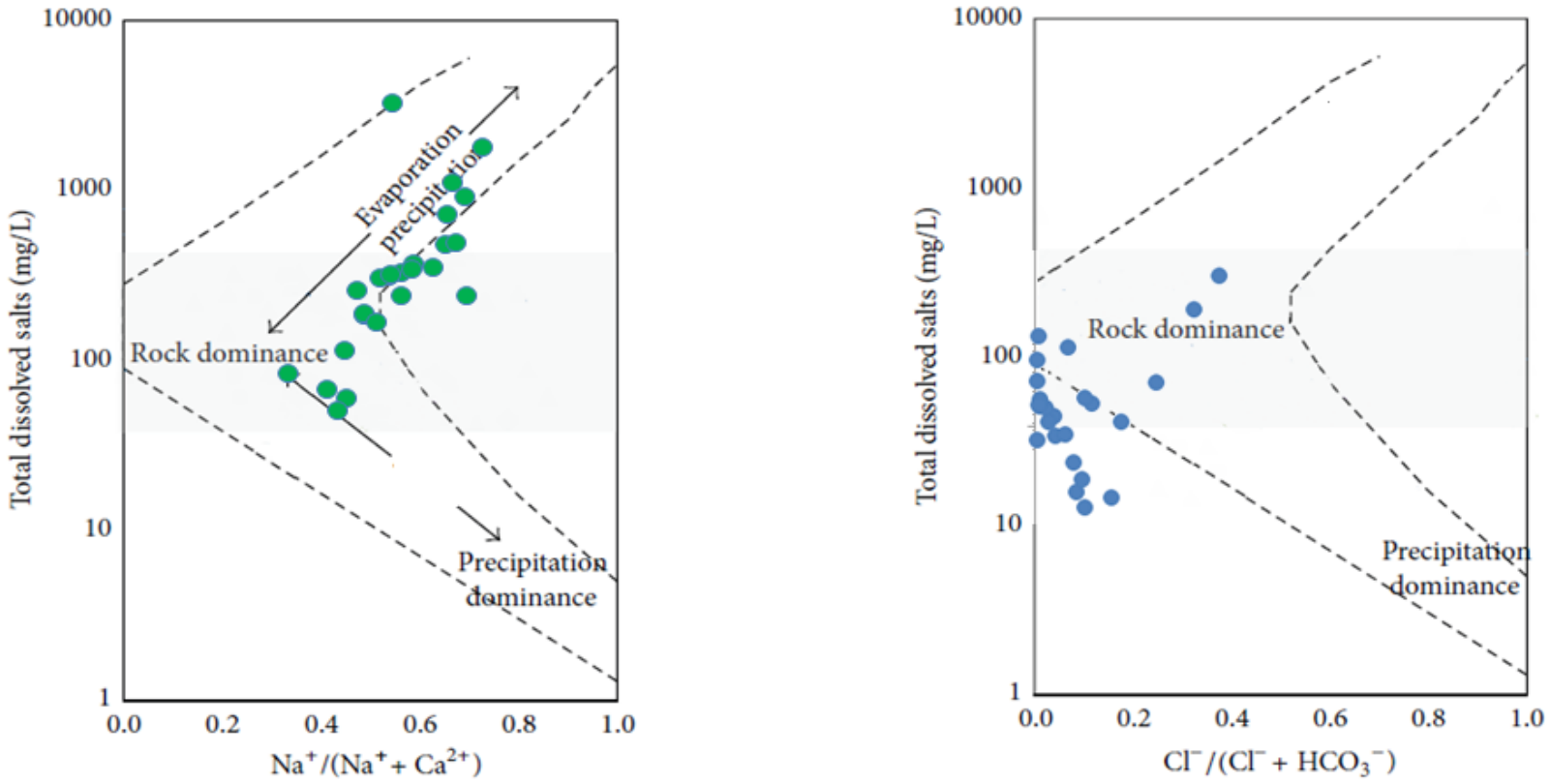
4.4 Hydrogeochemical processes behind groundwater quality

Gibbs plots were used to determine the hydrogeochemical processes influencing groundwater chemistry. According to results in Figure 9 a, rock dominance is the predominant process controlling groundwater chemistry in the wet season, accounting for 84 % of the groundwater chemistry. Precipitation and evaporation-crystallization contribute 4 and 12 % respectively in the wet season. The role of rock dominance in controlling groundwater chemistry decreases 72% of the boreholes; that of evaporation/crystallization increases to 28 % of the boreholes and declines to 0 % of the boreholes for precipitation.



(4) (b)

Figure 9: Gibbs plots showing processes affecting water chemistry in Tas Mwaulambya and Misuku based on: (a) TDS versus Na+/ (Na+ + Ca2+) wet season and (b) TDS versus Cl-/ (Cl- + HCO3-) wet season



(4) (b)

Figure 9: Gibbs plots showing processes affecting water chemistry in Tas Mwaulambya and Misuku based on: (a) TDS versus Na^{+}/ (Na^{+}+ Ca^{2+}) dry season and (b) TDS versus Cl-/ (Cl- + HCO3-) dry season

4.5 Isotopic content of groundwater

Figure 5 plots values of $\delta^{2}H$ against $\delta^{18}O$ for the sampled groundwater in the study area for the dry and wet seasons. The values of $\delta^{2}H$ and $\delta^{18}O$ ranged from -41.9 to -28.8 ‰ and from -6.3 to -4.6 ‰ averaging -35.77 and -5.68 ‰, respectively in the dry season (Figure 5). While in the wet season, they ranged from -42.0 to -29.0 ‰ and from -6.39 to -4.7 ‰ averaging -5.60 and -35.68 ‰ respectively (Figure 5).

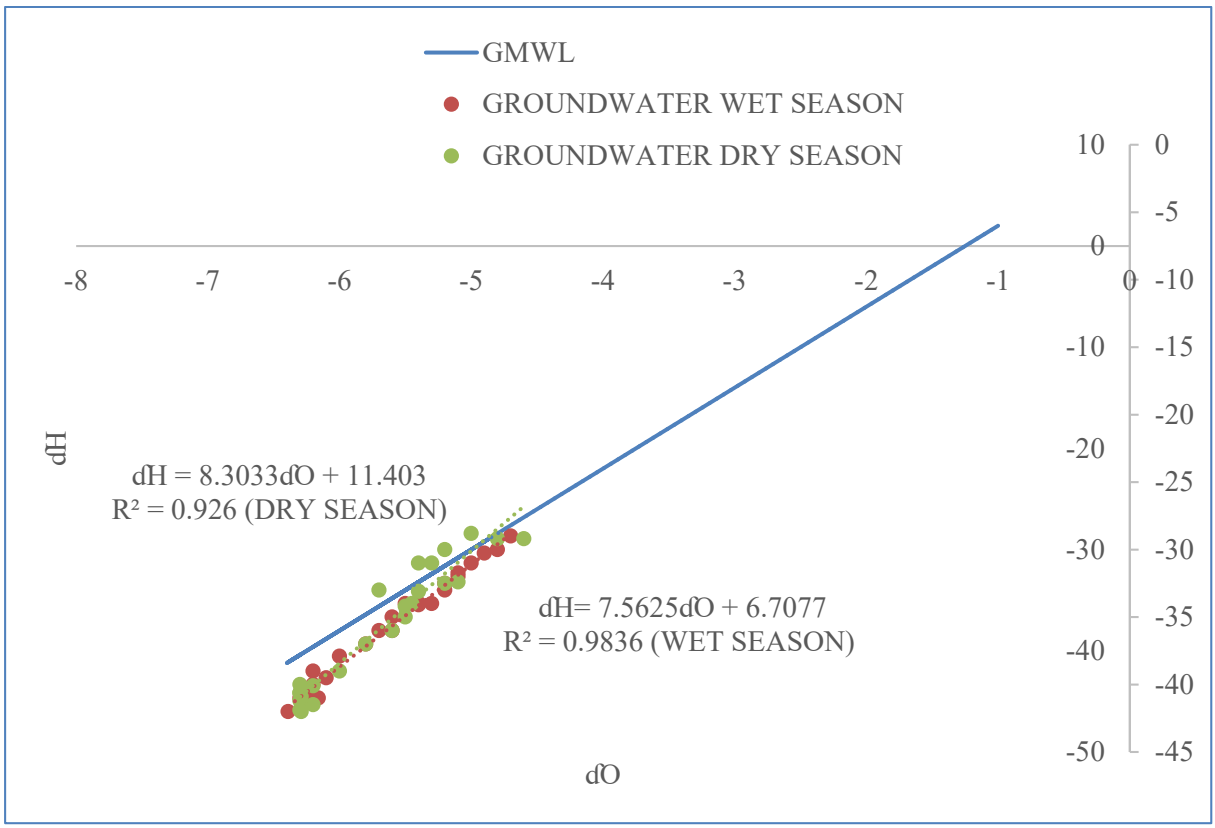


Figure 10: Isotopic plots of δ2H vs. δ18O for the wet and dry seasons

4.6. Seasonal Variations

Significant difference in levels of water parameters were determined through p – values at 95 % confidence interval (p = 0.05). p – values from the Students' t-test for seasonal variation of water quality parameters are presented in Table 5. Seasonal variation is shown in levels of EC, K^{+}, HCO_3, Cl^{-} and NO_3^{-}. pH, Na^{+}, Mg^{+2} and SO_4^{-2} levels show no seasonal variation. Seasonal variation is shown in 6 boreholes (24 %) in levels of Ca^{+2}.

Table 5: p-value for all water quality parameters in the study area

Borehole No.	p – values									
	pH	EC	Na^{+}	K^{+}	Mg^{+2}	Ca^{+2}	HCO_3^{-}	Cl^{-}	NO_3^{-}	SO_4^{-2}
BH 1	0.2	0.01	0.62	0.02	0.2	0.08	0.03	0.03	0.01	0.08
BH 2	0.75	0.04	0.2	0.02	0.1	0.1	0.03	0.03	0.01	0.1
BH 3	0.35	0.03	0.08	0.03	0.1	0.11	0.04	0.04	0.02	0.11
BH4	0.13	0.01	0.62	0.02	0.23	0.07	0.01	0.01	0.03	0.07
BH5	0.2	0.02	0.15	0.03	0.2	0.07	0.03	0.03	0.01	0.07
BH6	0.12	0.01	0.08	0.03	0.7	0.65	0.02	0.02	0.03	0.65
BH7	0.31	0.04	0.09	0.04	0.52	0.02	0.01	0.01	0.01	0.2
BH8	0.35	0.04	0.75	0.01	0.13	0.62	0.01	0.01	0.03	0.62
BH9	0.66	0.01	0.35	0.03	0.2	0.15	0.01	0.01	0.03	0.15
B10	0.1	0.01	0.13	0.02	0.12	0.08	0.02	0.02	0.04	0.08
BH11	0.28	0.02	0.08	0.01	0.33	0.09	0.01	0.01	0.01	0.09
BH12	0.08	0.03	0.1	0.01	0.03	0.06	0.01	0.02	0.03	0.67
BH13	0.1	0.02	0.11	0.04	0.06	0.91	0.02	0.01	0.02	0.91
BH14	0.11	0.03	0.07	0.03	0.1	0.01	0.01	0.03	0.01	0.2
BH15	0.07	0.04	0.07	0.01	0.75	0.1	0.03	0.03	0.04	0.2
BH16	0.07	0.02	0.65	0.02	0.35	0.02	0.03	0.04	0.03	0.75
BH17	0.65	0.03	0.2	0.01	0.13	0.75	0.04	0.01	0.02	0.35
BH18	0.2	0.03	0.62	0.02	0.2	0.01	0.01	0.03	0.01	0.13
BH19	0.62	0.03	0.15	0.01	0.12	0.13	0.03	0.03	0.01	0.2
BH20	0.15	0.04	0.08	0.04	0.31	0.02	0.04	0.04	0.04	0.12
BH21	0.08	0.04	0.09	0.04	0.35	0.17	0.01	0.01	0.04	0.31
BH22	0.09	0.01	0.62	0.04	0.66	0.31	0.03	0.03	0.03	0.35
BH23	0.12	0.03	0.01	0.01	0.1	0.35	0.02	0.02	0.01	0.66
BH24	0.91	0.02	0.04	0.02	0.06	0.66	0.01	0.01	0.03	0.1
BH25	0.2	0.01	0.09	0.03	0.1	0.01	0.01	0.01	0.01	0.09

NB: Blue = No significant difference; Red = Significant difference

CHAPTER FIVE: DISCUSSIONS

5.0 Introduction

This chapter explains the various factors that influence the results presented in chapter 4.

5.1 Physicochemical composition

5.1.1 Physical parameter

In the study area, the pH levels of the borehole water were between 6.2 to 7.5 in the two seasons. The recommended guideline values for pH in borehole water are: 6.5 to 8.5 according to WHO standards (WHO, 2023); and 6.0 to 9.5 per Malawi standards (MS733:2013), Thus water from all the sampled boreholes conformed to both international and national standards for pH in the borehole water. The conformity of borehole water to international standards is also reported by Chimphamba and Phiri, 2014. The pH levels of the groundwater demonstrate slightly acidic to slightly alkaline water. The acidity of the water is due to the formation of the bicarbonate and hydrogen ions when carbon dioxide combines with water to create carbonic acid, may contribute to this slight acidity per **Equation 9:**

$$CO_{2(g)+}H_2O_{(l)} \leftrightarrow HCO^-_{3(aq)} + H^+_{(aq)} \text{ Equation 9}$$

The electrical conductivity (EC) of water is caused by the presence of dissolved solids in water. EC is correlated to total dissolved solids (TDS), $R^2 = 1$ in this study. The maximum permissible limits for EC and TDS in borehole water are: 3500 μS/cm and 2000 ppm respectively according to the Malawi standards; 3000 μS/cm and 1500 ppm per WHO standards. In the study area, the EC values ranged from 4.7 μS/cm to 1363 μS/cm while TDS levels varied from 2.82 to 636 ppm. These values indicate that the water in the study area conforms to the international and national standards for EC and TDS. Further water with TDS levels below 1000 mgL^{-1} is considered suitable for consumption, while water with TDS levels above 1000 mgL^{-1} is considered brackish and unfit for drinking. It's worth noting that areas with higher EC values in water could be influenced by factors such as evaporation and human activities, including agriculture. Additionally, the higher EC values may be associated with the water's extended residence time and the geological characteristics of the region.

The Final Report: Part I Existing Conditions in the Project of National Water Resources Master Plan in the Republic of Malawi classifies Malawi aquifers into three categories: Quaternary alluvial, weathered basement, and fractured basement aquifers. TAs Mwaulambya and Misuku

in Chitipa district lie in the zone containing a weathered basement aquifer per this report. The weathered basement aquifers are characterized by low EC due to the limited mineralization of underlying rocks (Smith-Carrington and Chilton, 1983). Typical EC values for these aquifers are less than 1500 µS/cm. Thus, EC values from this study agree with these earlier researchers.

5.1.2 Chemical parameters

Different levels of cations and anions were obtained in the sampled boreholes in TAs Mwaulambya and Misuku in Chitipa district during both seasons. The levels of cations were in the order $Na^{+} > Ca^{+2} > K^{+} > Mg^{+2}$. For anions, the trend was: $HCO_3^{-} > Cl^{-} > SO_4^{-2} > NO_3^{-}$. Such trends in cations and anions composition of groundwater in weathered basement aquifers are reported in the literature (Chimphamba and Phiri, 2014; Wanda et al., 2011; Smith–Carlington and Chilton, 1983; Bath, 1980).

Sodium can occur naturally in groundwater from rock weathering in the aquifers as well as through infiltration from sewage and industrial wastewater. The maximum permissible sodium content for groundwater, according to both Malawi and WHO standards is 200 mgL^{-1}. The measured sodium concentrations during the dry and wet seasons ranged from 10 to 69 mgL^{-1} as such all the borehole water samples in both seasons met the standard for sodium in borehole water. The typical concentration of sodium in weathered sediment aquifers is 5 – 70 mg/L (Smith–Carlington and Chilton, 1983) thus the results from this study agree with what is reported in the literature. Similar sodium levels are reported for Chitipa district by Chimphamba and Phiri, 2014.

Calcium in groundwater originates from highly soluble calcium-rich minerals, such as limestone and gypsum. In addition, runoff from agricultural fields in the wet season may add calcium to the groundwater through infiltration since some fertilizers such as calcium ammonium nitrate (CAN) contain calcium. (5.3 %). Calcium concentrations in the studied area for the two seasons ranged from 6.2 to 13.9 mgL^{-1}. The maximum permissible limit set for calcium in borehole water is 250 mg/L as such all the borehole water samples conformed to the national standards. The typical calcium concentration in weathered sediment aquifers is 10 – 100 mg/L (Smith–Carlington and Chilton, 1980); thus, the results from this study agree with what is reported in the literature. Similar calcium levels are reported for the neighboring district of Karonga by Ward et al. (2020).

In the studied area, the concentration of potassium ranged from 1.45 to 5.8 mgL^{-1} in the dry season. In the wet season, the range was 3.1 to 7.8 $mgL^{-}1$. These values are less than the maximum permissible value of potassium (50 mg/L) according to WHO and Malawi standards. Smith–Carlington and Chilton, 1983 report less than 6.0 mg/L potassium in weathered basement aquifers, thus our findings apart from 6 boreholes (%) agree with what is reported in the literature. The increased potassium levels may be attributed to agricultural runoff since the boreholes occur in areas of intensive agriculture and that the high levels are recorded for the wet season. Low levels of potassium are contained in groundwater because the rocks it originates from are highly resistant to weathering (Carter and Burnett, 1975). However, runoff from agricultural fields through infiltration may increase potassium levels in groundwater since NPK fertilizers contain potassium (5 % K_2O), and higher levels are reported in the wet season.

The concentration of magnesium in the studied area for the two seasons ranged from 2.42 to 62.8 mgL^{-1}. The maximum permissible levels of magnesium in drinking water are 50 and 200 mg/L according to WHO and Malawi standards respectively. Thus, all the boreholes conformed to the international and national standards for magnesium except BH 12 which does not conform to the WHO standards. Magnesium in groundwater may arise from the mineralization of rocks such as dolomite and runoff from agricultural fields where fertilizers such as CAN are applied (NGWA, 1999). Together with calcium, magnesium contributes to the hardness of water.

Carbonate levels in all the sampled water samples were found to be 0.00 mg/L. This is expected since carbonate can only be detected at water pH greater than 8.4. Bicarbonate levels varied from 40.2 to 194 mgL^{-1} in the two seasons. No guideline values for bicarbonate are set in the WHO and national standards. The presence of bicarbonate ions in the water may be attributed to the dissolution of carbon dioxide in the water per equation 9. The large variation in levels of bicarbonate is attributed to the instability of the bicarbonate anion. Smith-Carlington and Chilton, 1983 report a range of 100 – 500 mg HCO_3^-/L for borehole water in weathered basement aquifers and all the boreholes in the dry season except BH 18 had bicarbonate levels outside this range (< 100 mg/L). In the wet season, 18 boreholes (72 %) recorded bicarbonate levels within the reported range. The data from Smith-Carlington, 1983 is quite old, nevertheless water quality for northern Malawi is scanty as pointed out by Holm et al., 2018. And although groundwater quality studies have been done by several researchers: Chidya et al.

(2018); Wanda *et al*. (2011), etc. these studies were done in Mzuzu City and Mzimba and their results compare well with our findings.

Chloride lies in the range of < 20 mg/L in boreholes from weathered basement aquifers (Smith-Carlington and Chilton, 1983). The findings of this study adhere to this range except BH 11 and 12 in both seasons; and BH7 and BH 10 in the wet season. The findings recorded higher levels of chloride at these boreholes. The measured chloride concentrations ranged from 0.3 to 59 mgL^{-1} during the dry season and from 0.3 to 59 mgL-1 during the wet season. Infiltration of polluted groundwater from pit latrines may have led to high levels of chloride in the water since the boreholes were located in densely populated areas. The chloride levels were then the maximum permissible limits for chloride as set out in the WHO and Malawi standards (200 and 750 mg/L).

The sulphate concentrations in the study area ranged from 3.1 to 40.3 mgL^{-1} during the dry season. During the wet season, sulphate concentrations ranged from 3.1 to 39.6 mgL^{-1}. The WHO recommended sulphate level is 400 mgL^{-1}, while Malawi's drinking water standard is 800 mgL^{-1}, hence all the sampled boreholes conformed to the standards. Sulphates are usually present in groundwater at low concentrations however high levels of sulphates are reported in alluvial aquifers of the Lower Shire in Malawi (up to more than 900 mg/L; Monjerezi *et al*., 2011). Smith-Carlington and Chilton, 1983 report ranges of 5 – 100 mg/L for weathered basement aquifers.

Nitrates in water can come from various sources: oxidation of atmospheric nitrogen followed by dissolution of the nitrogen oxide in atmospheric moisture; nitrogen fixation by leguminous plants; decay of plant and animal matter; animal waste; agricultural runoff and industrial wastewater. The measured nitrate levels during the dry season ranged from 0.7 to 9.1 mgL^{-1}. During the wet season, nitrate levels ranged from 0.3 to 68.6 mgL^{-1}. All boreholes except BH 12 in the wet season had nitrate values below the WHO and Malawi maximum standard of 45 mgL^{-1}. The levels of nitrate in weathered basement aquifers are low (< 5 mg/L) and this is shown in 20 boreholes (80 %) and 17 boreholes (68 %) in the dry and wet seasons respectively. The boreholes with high nitrate levels were suspected to be contaminated with human and/or animal excreta. High nitrate levels can also be attributed to agricultural runoff from heavily fertilized farms in the vicinity of the boreholes.

5.2 Ion Charge Balance Errors of Groundwater Quality

The results of this analysis on chemical parameters were authenticated using the charge balance, E for each borehole in each season as presented in Table 3 It is noted that: -5 % ≤ E ≤ 5% for all boreholes in each season. Such magnitudes for E are indicative of water that is electrically neutral and points to acceptable standards of chemical analysis.

5.3 Groundwater Classification

The groundwater classification in this study area was based on Piper diagrams. The groundwater was mainly found to be of mixed types: namely Ca-Na-HCO_3 and Ca-Mg-SO_4. The dominant cation was found to be Na^+, indicating probable cation exchange where high levels of Ca^{+2} are exchanged for Na^+ over Mg^{+2}. It was also observed that there is a higher presence of magnesium (Mg) compared to calcium (Ca). The major anion is bicarbonate, which can be attributed to the presence of calcite, dolomite, rhyolite, and basalt minerals. These findings are consistent with what is reported by other researchers in the northern region (Ward et al., 2020; Wanda et al., 2011).

The Piper plots help in understanding the hydrochemical properties of water and provide insights into the relative proportions of major ions. They also highlight variations in hydrological conditions and water sources between wet and dry seasons. During the wet season, there is typically more surface runoff and increased groundwater recharge, leading to higher concentrations of dissolved ions in the water. The most abundant alkali metal is Na^+, which can be contributed by sources such as rock salt weathering and silicate minerals. The dissolution rate of Na^+ is higher than that of K^+, resulting in higher Na^+ content. Ca^{+2} is observed as the most abundant alkaline earth metal, while Mg^{2+} can be derived from sources like dolomite and weathering ferromagnesium minerals.

Overall, the concentrations of major ions vary between wet and dry seasons. During the wet season, leaching from soils and rocks contributes to higher concentrations of dissolved substances. Conversely, during the dry season, water evaporation and lower groundwater levels lead to higher concentrations of ions. Human activities, such as irrigation and agricultural practices, can introduce additional ions into groundwater throughout the year.

It's worth noting that the geological parameters of the area also play a role in the hydrochemical characteristics of groundwater. The movement of water through different geological formations can influence the ion composition. For example, water flowing through syenite alkali rock can

result in high concentrations of potassium, sodium, and calcium ions. Dolomites, pegmatitic veins, and karoo rocks can also be significant sources of cations and anions in underground water.

However, it's important to consider that the variations observed in the Piper plots between wet and dry seasons were not very significant in this study. Longer seasonal variations and a broader range of activities can impact the overall ion composition and subsequently affect the Piper plot diagram.

5.4 Hydrogeochemical processes behind groundwater chemistry

From the Gibbs plot, rock dominance was found to be the main process behind groundwater chemistry in the study area. Bath (1980); and Smith-Carlington and Chilton (1983) have also pointed out that the lithology of the aquifers in basement aquifers controls their groundwater chemistry. The abundance of dissolved ions in groundwater depends on the presence and solubility of ions in the underlying rock (Saha *et al.,* 2019). Evaporation becomes a little bit more significant in controlling groundwater chemistry during the dry season (18 % of boreholes vs 4 % of boreholes in the wet season) due to higher temperatures and reduced water availability from precipitation. Precipitation on the other hand played no role in groundwater chemistry at all in the dry season, which is anticipated given that no rains are received in the study area in the month of October when the samples were collected. Lanjwani and Khuhawar (2020) have attributed rock dominance, evaporation, and precipitation to the control of groundwater chemistry.

In this study area of Chitipa, as water evaporates, lighter isotopes preferentially evaporate, resulting in an enrichment of heavier isotopes in the remaining water. Prolonged evaporation can lead to higher values of $\delta^{2}H$ and $\delta^{18}O$ in groundwater. Additionally, the dry season is characterized by lower precipitation and reduced groundwater recharge. Limited rainfall means less input of fresh isotopically light rainwater into the aquifer. Consequently, groundwater during the dry season tends to have higher values of $\delta^{2}H$ and $\delta^{18}O$ compared to the wet season.

With high precipitation in the wet season, there is increased recharge of groundwater aquifers. Rainwater, with its distinct isotopic signature, infiltrates the ground and mixes with existing groundwater, causing a decrease in isotopic values. This is consistent with the increased concentration of ions like calcium, potassium, chloride, and nitrates that are washed away from

fields and pit latrines. The influx of rainwater dilutes the existing groundwater, resulting in lower δ^2H and $\delta^{18}O$ values that are more like the isotopic signature of rainwater.

The isotopic composition of hydrogen and oxygen in precipitation is an important tool for analyzing water within the hydrological cycle. In the studied area, there were no significant differences in the isotopic compositions between the wet and dry seasons. The readings aligned with the global water lines, suggesting no deviations. The correlations between the δ^2H and $\delta^{18}O$ compositions during the dry season were like those of the rainy season but with a higher intercept, indicating a greater deuterium excess. This could be attributed to various land surface-atmosphere interactions influencing rainfall in the area. The isotopic readings in different seasons could suggest various moisture sources contributing to precipitation in the research area.

The regression equations for the isotopic composition of groundwater samples in the dry season and wet seasons are: $\delta^2H = 8.3033\ \delta^{18}O + 11.403$ and $\delta^2H = 7.5625\ \delta^{18}O + 6.7077$ respectively. Given that the Global Meteoric Water Line is: $\delta^2H = 8\delta^{18}O+10$ the plots in Figures 5 and 6 confirm that the groundwater from the study areas is of meteoric origin. The R^2 values for the dry and wet seasons are 0.926 and 0.9836 respectively. Thus, the wet season isotopic plot is more collinear with the GMWL than the dry season isotopic plot. This entails a greater contribution of rainfall to the groundwater resources in the wet season compared to the dry season. Furthermore, studies by Banda *et al.* (2019) and Monjerezi *et al.* (2011) in the central and southern regions of Malawi also show that groundwater sources in the country are of meteoritic origin.

5.5 Seasonal Variations

Temperature, EC, TDS, and pH offered contrasting trends as regards seasonal variation. It was noted that there was no significant variation in levels of pH between the dry and wet seasons ($p > 0.05$). pH in water is affected by carbon dioxide concentration in water, temperature, carbonate and bicarbonate concentrations in the water, and organic material decomposition. Of the four factors the last, organic material decomposition would lead to seasonal variation of pH in the study area as organic manure is under use in the rainy season to fertilize the farms in the vicinity of the boreholes. Organic matter upon decomposition followed by nitrification releases NH_4^+ which adds H^+ ions to the water (Gonzalez *et al*., 2002). This would tend to decrease the water pH. However, such a trend is not observed. This was attributed to a considerable amount of the alkalinity of the water (>20 mg/L) for all samples. High alkalinity has a buffering effect

on the water so that the pH does not change although H^+ is added or removed from the water (Hagens *et al*., 2020). Studies in other parts of the region, Mzimba showed seasonal variation in pH (Ward *et al*., 2020).

EC which is positively correlated to TDS shows seasonal variation at all the sampled boreholes ($p < 0.05$).

Furthermore, there is no fixed tendency of decrease or increase from the dry season into the rainy season for the EC. The EC decreases from dry into the rainy season at 11 boreholes (44 % of the boreholes). The decrease in EC levels may be due to the 'dilution effect' arising from the rainwater that percolates into the groundwater (Alilouch *et al*., 2017). EC at 14 boreholes (56 %) recorded higher values for the rainy season compared to the dry season. The increased EC for the rainy season has a corresponding increase in the ion concentrations of the major ions (Cl^{-1}, HCO_3^{-1}, NO_3^{-1}, K^{+1}, Mg^{+2}, and Ca^{+2}). Therefore, the EC was correlated to each ion to determine which one had the most effect on it. The correlation coefficient was in the order $NO_3^{-1} > Cl^{-1} > K^{+1} > Mg^{+2} = Ca^{+2} > HCO_3^{-1}$ (0.88, 0.77, 0.69, 0.59, 0.49, and 0.10 respectively. This shows that nitrate and chloride are the major contributors to the increased EC. The immediate environmental setting of each borehole was consequently analyzed to ascertain what led to increased ion concentration in the rainy season. It was suggested that the chloride was of domestic origin, pit latrines while the nitrate arose both from homes and farms. This is consistent with the literature, by Gonzalez et al. (2002) which suggests human waste and fertilizers as sources of NaCl and nitrate pollution in water. Studies by Ward *et al*., 2020 also noted seasonal variation in EC in other northern parts of Malawi.

Amongst the chemical parameters, seasonal variation was shown in the levels of potassium, chloride, nitrate, and bicarbonate ions ($p < 0.05$); mainly due to agricultural runoff from farms in the vicinity of the boreholes and due to the infiltration from pit latrines (chloride) that add the ions to the borehole water in the wet season. This is evidenced by the fact that the levels of the ions increase during the wet season (56 %). The increase in the concentration of these ions from the wet into the dry season is accounted for by 'the concentrating effect of evaporation on aquifers' (Monjerezi *et al*., 2011). No significant difference in levels of sodium, calcium, magnesium and sulphate is shown in the sampled borehole water. Similar trends in seasonal variation are reported in the literature for the northern part of Malawi (Mapoma and Xie, 2014).

CHAPTER SIX: CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions and Recommendations

The present study has found out the following about the groundwater from boreholes in TAs Mwaulambya and Misuku in Chitipa district: The isotopic modeling showed that the water originated from atmospheric precipitation. The isotopic plots for both seasons lie along the GMWL but the plot for the wet season is more collinear with the GMWL. There is no seasonal variation in levels of pH, sodium, sulphate, calcium, and magnesium while levels of electrical conductivity, nitrate, chloride, bicarbonate, and potassium showed seasonal variation. Electrical conductivity, nitrate, chloride, bicarbonate, potassium, and calcium showed a statistically significant increase ($p<0.05$) from the dry season into the rainy season because of infiltration and increased rock dissolution. The hydrochemical modeling showed that the aquifers in the study area were predominantly rocks rich in alkali metals, bicarbonate, and chloride minerals. However, 40% of boreholes showed the presence of alkali earth metals in the aquifers. Human activities and rock weathering were found to be the predominant processes controlling groundwater chemistry. Human activities become more prominent in the rainy season compared to the dry season.

From the findings of the present study, it is recommended that: Good agricultural practices be followed to minimize agricultural runoff that may eventually infiltrate into the aquifers thereby causing nitrate pollution. Pit latrines be constructed according to the set sanitary practices that would prevent infiltration of sodium and chlorides into the aquifers. As part of integrated resources water management afforestation of the study area should be intensified and sustained to ensure reliable rainfall which is the main recharge process of the aquifers. In addition, afforestation maintains adequate vegetative cover preventing soil erosion whilst ensuring the percolation of rainwater into the aquifers, replenishing them as water is being abstracted. This prevents the drying up of boreholes.

6.2 Way forward

As a follow-up to the present study: Similar studies should be undertaken over extended periods within seasons in other traditional authorities within Chitipa, viz: Kameme, Wenya, and Nthalire to assess seasonal variability of water quality parameters. This will create baseline data on the water quality for the entire district. Such data is lacking in the reviewed literature. Isotopic studies should be carried out to determine the origins of groundwater in the other TAs.

The studies could be extended to other isotopes such as carbon – 13 at PhD level. Hydrochemical modeling be done in these other TAs to find out the main minerals in the aquifers in the TAs. Similar studies be carried out in the other TAs in the district to determine what processes control the groundwater chemistry.

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APPENDICES

APPENDIX 1: Ethical Clearances

MZUZU UNIVERSITY RESEARCH ETHICS COMMITTEE (MZUNIREC)

Ref No: MZUNIREC/DOR/21/56 23rd Nov., 2021

Mr. Watson Kabaghe,

Mzuzu University,

P/Bag 201,

Mzuzu.

Email:wkabaghe@unilia.

acmw

Dear Mr. Watson Kabaghe,

RESEARCH ETHICS AND REGULATORY APPROVAL AND PERMIT FOR PROTOCOL REF NO. MZUNIREC/DOR/21/56: HYDROGEOCHEMICAL MODELLING AND ISOTOPIC COMPOSITION AS TRACERS OF POLLUTION AND GROUND WATER RECHARGE IN CHITIPA DISTRICT, MALAWI

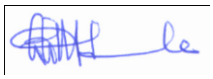
Having satisfied all the relevant ethical and regulatory requirements, I am pleased to inform you that the above referred research protocol has officially been approved. You are now permitted to proceed with its implementation. Should there be any amendments to the approved protocol in the course of implementing it, you shall be required to seek approval of such amendments before implementation of the same.

This approval is valid for one year from the date of issuance of this approval. If the study goes beyond one year, an annual approval for continuation shall be required to be sought from the Mzuzu University Research Ethics Committee (MZUNIREC) in a format that is available at

the Secretariat. Once the study is finalised, you are required to furnish the Committee with a final report of the study. The Committee reserves the right to carry out compliance inspection of this approved protocol at any time as may be deemed by it. As such, you are expected to properly maintain all study documents including consent forms.

Wishing you a successful implementation of your study.

Yours Sincerely,

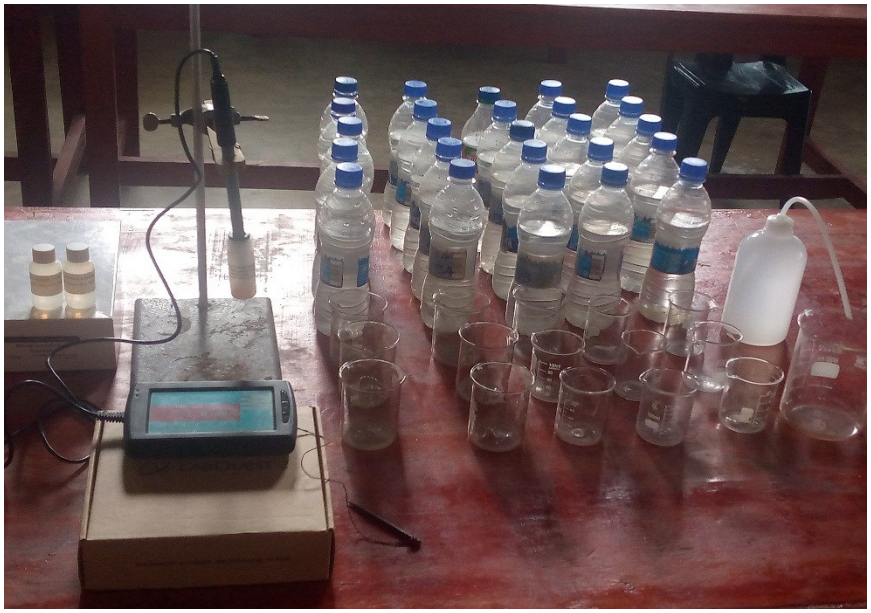


Gift Mbwele

MZUZU UNIVERSITY RESEARCH ETHICS ADMINISTRATOR

For: CHAIRMAN OF MZUNIREC

APPENDEX 2: Pictures for sample collection and sample analysis



APPENDIX 3: GPS Values for the sampling points.

SAMPLING POINT	ALTITUDE	LONGITUDE	LATITUDE
BH1	1323	513241	8943884
BH2	1311	512660	8943939
BH3	1322	514686	8945010
BH4	1319	514334	8944697
BH5	1306	514318	8945158
BH6	1328	514945	8944757
BH7	1304	514992	8945688
BH8	1299	515101	8945853
BH9	1330	515915	8944748
BH10	1314	515251	8945507
BH11	1281	519236	8949270
BH12	1310	524357	8946475
BH13	1330	547057	8919894
BH14	1292	546110	8919890
BH15	1257	544084	8923587
BH16	1245	539632	8926036
BH17	1253	538763	8926036
BH18	1165	557066	8921105
BH19	1234	557056	8919562
BH20	1288	553897	8918846
BH21	1349	550319	8918881
BH22	1353	549800	8919044
BH23	1346	549484	8919464
BH23	1312	548776	8919564
BH25	1336	549441	8918321