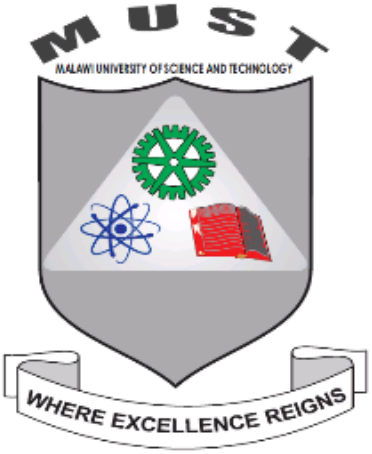


HYDROGEOCHEMICAL ASSESSMENT OF GROUNDWATER BASED ON AQUIFER LITHOLOGY AROUND NCHALO, CHIKWAWA

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Dissertation submitted to Ndata School of Climate and Earth Sciences of the Malawi University of Science and Technology in partial fulfillment of the requirements for the Bachelor of Science degree in Earth Sciences (Geology).

July 2021

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ABSTRACT

This study focused on analyzing and correlating the chemical composition of groundwater to aquifer lithology, in an area underlined by superficial (alluvial) deposits with subsurface extensions of Cretaceous Lupata sediments and Basement complex. To achieve the main objective, the following specific objectives were carried out: (1) to analyze and interpret the water quality parameters of groundwater resource sample data; (2) to determine hydrogeochemical water types of each sampled groundwater resource; and (3) to use HCA and PCA to divide groundwater samples into different groups. Multivariate statistical analyses (PCA and HCA) combined with Piper trilinear graphical analysis were used to assess groundwater quality and understand the local hydrogeology on the groundwater hydrochemistry,

The study involved collecting 8 groundwater samples from 4 different borehole sites. The analytical results of groundwater chemistry indicated that the order of abundance of cation concentration was Ca>Na>Mg>K, while those of anions were HCO_3>SO_4>Cl. The hierarchy cluster analysis (HCA) transformed the groundwater samples into three groups, and principal component analysis (PCA) identified that the major chemical variables governing PC1 and PC2 were (Ca, Mg, K, SO_4, HCO_3) and Cl respectively, and these explained most of the hydrogeochemistry. The hydrogeochemical facies observed from the piper plot were mostly of Ca-HCO_3 types whereas some were of mixed Ca-HCO_3-Cl type. These facies were seen to have originated from aquifer lithology through (1) the water-rock interactions to the phases of carbonate rocks (i.e. limestone and dolomites), gypsum, evaporate minerals (halite), calcite, silicates, and mafic minerals; (2) ion-exchange between Ca and Mg with Na in clayed sediments; and (3) mixing with fresh water. Generally, the groundwater is slightly saline or blackish and can be safe for human consumption. For further studies, the determination of seasonal variations of hydrogeochemical parameters in these groundwater resources is recommended.

ACKNOWLEDGEMENTS

First and foremost, I sincerely give the Almighty God all glory for granting me sound health, strength, and determination to undertake this study.

I would like to express my appreciation and gratitude to my supervisor, Ms. E. C. Mabedi, for her guidance, and endless support, always finding time and patience for advising me in this research. I thank my parents for their encouragement and financial support, and also not forgetting my friends for their warm academic company and consultations during this work.

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ACRONYMS/ABBREVIATIONS

MBS: Malawi Bureau of Standards

WHO: World Health Organization

TDS: Total Dissolved Solids

EC: Electrical Conductivities

PCA: Principal Component Analysis

HCA: Hierarchy Cluster Analysis

MBC: Malawi Basement Complex

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CHAPTER 1: INTRODUCTION

1.1. Background

In sub-Saharan countries, most communities depend on groundwater as their vital source of domestic water supply, as it is cheap and safe (Nyika & Onyari, 2019; Sidibe, Lin, & Kone, 2019). In Malawi, especially in the lower shire river valley, groundwater resource is deemed as the most reliable water supply to meet the ever-increasing water demands in the region. However, the dependence on this deemed water source is limited due to quality degradation which calls for assessment and mitigation or remedial measures.

Groundwater quality issues like salinization are a major concern for human health as well as for water resources development projects. According to Abreha (2014); Wu, Chen, & Zhang (2015); and Nyika & Onyari (2019), the major processes that determine groundwater chemical composition are; atmospheric inputs, inputs of chemicals by human activities, and geological features and processes within the aquifer. The interaction of all these factors leads to various water types and gives important clues for the geological history of the enclosing rocks (Freeze & Cherry, 1979). Hydrogeological environments and element compositions of groundwater are vital constraints and limiting aspects for development. Hence, it is important to understand the origin of concentrates, hydrogeochemical processes, and their evolution that take place in both ground and surface water resources (Abreha, 2014).

A review of the literature shows that closely no attempts have been made to study the hydrogeochemical processes and evolutions that govern the groundwater chemistry and origins of the water although water quality issues (i.e. salinity) are the main concern in the studied area, Nchalo. Hence, the paper aims to study the extent to which aquifer geology or lithology of aquifer influences the hydrogeochemistry of groundwater resources around the Nchalo area.

1.2. Research problem

Most groundwater resources around Nchalo have been recorded for potential high salinity levels (Gebretsadik, 2010; Sehatzdeh, 2011; Monjerezi, Vogt, Aagaard, & Saka, 2012). Even though there is a major concern on water quality issues in the area, researches on hydrogeochemical and water quality studies are scanty. As a result, the hydrogeochemical processes (evolution), origins, mixing, and quality of the water resources in the Nchalo area are not well known. Besides, the source of element concentrations and susceptibility of the water resource to pollution is not well understood. This causes a large uncertainty in understanding the major hydrogeochemical processes governing the evolution of water chemistry.

Therefore, this study aimed at analyzing the chemistry of groundwater resources in or around the Nchalo area to determine if the geology or lithology of the aquifer(s) in the study area is influencing the present groundwater hydrogeochemistry.

1.3. Research objectives

1.3.1. Main Objective

This research aimed to analyze the groundwater chemistry of the area around Nchalo and correlate the obtain hydrogeochemistry to the lithology of an aquifer in the study area.

1.3.2. Specific Objectives

The specific objectives were;

- To analyze and interpret the water quality parameters of groundwater resource sample data
- To determine hydrogeochemical water types of each sampled groundwater resource
- To identify possible hydrogeochemical processes controlling water quality

1.4. Research questions

The study answered the following research questions;

- To what extent or how does the geology or lithology of aquifer influence the hydrogeochemistry of groundwater resources in the study area?
- What are the key hydrogeochemical processes affecting water quality in the

area?

- Are the sampled groundwater resources being tapped from the same aquifer?

1.5. Significance of study

The study makes a significant contribution to the quality of groundwater resources in the Nchalo area, both in addressing the gap in knowledge on the major processes influencing the chemistry of the groundwater and in highlighting the correlation of lithology of an aquifer to water type in the area. The findings from the study will provide baseline scientific data for the sustainable management of groundwater resources in the study area.

1.6. Organization of the thesis

The research is organized into five chapters.

Chapter 1: Contains the introduction of the research that includes the background, research problems, objectives of the research, research questions, and the significance of the study.

Chapter 2: Deals with the literature review

Chapter 3: Presents a brief introduction of the study area description, hydrogeology, and geology. It is also devoted to the method of data collection and analysis.

Chapter 4: This chapter presents the main findings of the study. Results and discussion include illustration and discussion of general hydrogeochemistry, hierarchical cluster analysis, principal component analysis, and piper diagram.

Chapter 5: The last chapter concludes by presenting the main issues discussed in this study as well as by providing recommendations for further improvement and researches.

CHAPTER 2: LITERATURE REVIEW

2.1. Introduction

This chapter highlights the existing literature and gives an overview of the present research in hydrogeochemical processes and groundwater quality. For better understanding, the literature review will be based on the following topics: General concept of hydrogeochemical assessment; source and occurrence of ions in water; methods to assess water quality; and reviews of studies and work.

2.2. The general concept of hydrogeochemical assessment

According to Nagaraju, Thejaswi, & Sreedhar (2016), groundwater is one of the earth's most important resources for human life whose quality depends on various chemical constituents and their concentration, which are mostly obtained from the geological data of the specific area. Naturally, the chemical composition of groundwater in most cases is influenced by the lithology of an aquifer in a particular area. Hydrogeochemical studies are usually conducted to investigate the processes that occur in water bodies (surface and groundwater) and affect the water quality (Rao, et al., 2017). The investigation and assessment of groundwater chemistry and quality is a hot topic worldwide, triggering international attention from both researchers and policy makers due to its relevant link with environmental objectives and regional development (Saha, Selim Reza, & Roy, 2019; Chai, Changlai, Li, & Liang, 2020).

Hydrogeochemical assessment involves the chemical analysis of groundwater: (1) to identify and quantify chemical constituents and their concentration; (2) to identify or come up with processes that influence the general composition of groundwater; and (3) to determine the origin and evolution of the groundwater in terms of its chemical composition, and sometimes relating this to the local geology of a particular region. Srinivasamoorthy et. al (2014) and Canora, Rizzo, Panariello, & Sdao (2019), emphasized that the hydrogeochemistry of any groundwater is heavily dependent on water recharge, water-rock interaction along flow paths, dissolution of basement rocks, groundwater mixing due to different aquifers, and anthropogenic sources. The hydrogeological and groundwater hydrogeochemical assessments have primary importance to define the hydrogeological conditions of the systems for implementing sustainable integrated management of groundwater (Li, Wu, Qian, & Gao, 2018).

2.3. Source and occurrence of ions in groundwater

The natural composition of groundwater chemistry is described through the relative abundance of t

Saveca (2016) explains that the natural source and concentration of chemical ions, as well as the range of mentioned ions in the groundwater, are rock minerals. The interaction between this rock mineral with recharge water usually controls the natural quality of groundwater through different hydrogeochemical processes. During the interaction between the geological environment and recharge water, the rock minerals are dissolved and transported to groundwater in ionic form through infiltration and percolation.

2.4. Reviews of studies and work in Malawi

In Malawi, various authors have conducted hydrogeochemical assessments of groundwater resources in different locations, Lower Shire Valley inclusive. Monjerezi et. al (2011) assessed the major ion chemistry and salinity of groundwater to determine the dominant hydrogeochemical processes controlling groundwater chemical composition in an area with saline groundwater in the Lower Shire Valley, and they incorporated the methods of water quality assessment such as hierarchy cluster and principal component analyses. Monjerezi et. al (2012) went further on to conduct another study in the Lower Shire Valley where they employed more conceptually based hydrogeochemical assessment techniques and models to assess the empirical processes controlling groundwater chemical composition. Nyirenda et. al (2015) investigated the hydrogeochemical characteristics, determined the water-rock interaction influencing the water quality, and assessed the quality of groundwater for direct human consumption and irrigation uses in Salima and Nkhotakota districts. Missi (2018) analyzed the chemical composition of groundwater and surface water to determine their evolution as well as their relationship to water-rock interactions, and how they are affecting the water quality in the Lake Chilwa Basin.

Although these studies have been conducted, the authors only conducted the hydrogeochemical assessment studies to a large areal extent (gives general overview), but not to a limited extent like in a specified small area. Conducting hydrogeochemical assessment studies on a local or specified small area tends to produce more detailed results that may not have been encountered during regional or large areal extent studies. Due to this fact, most limited areal extents with significant groundwater quality

deterioration issues are not carefully studied to assess their chemical composition and their influen

CHAPTER 3: METHODOLOGY

3.1. Research design

This research project mainly focused on the experimental part of water quality assessment. This initially involved the process of determining the reliable groundwater resources of the studied area (sampling points) using purposive sampling, to select villages to sample from. Then, the second part involved desk-work study, sample collection, and recording of GPS coordinates. The major ions or chemical parameters of the sampled groundwater were tested using proper instruments, and different software such as GW_Chart and PAST software to analyze the data obtained. The obtained measurements were later on compared with those of the MBS and WHO, and also with the type of aquifer lithology in the studied area.

3.2. Study area

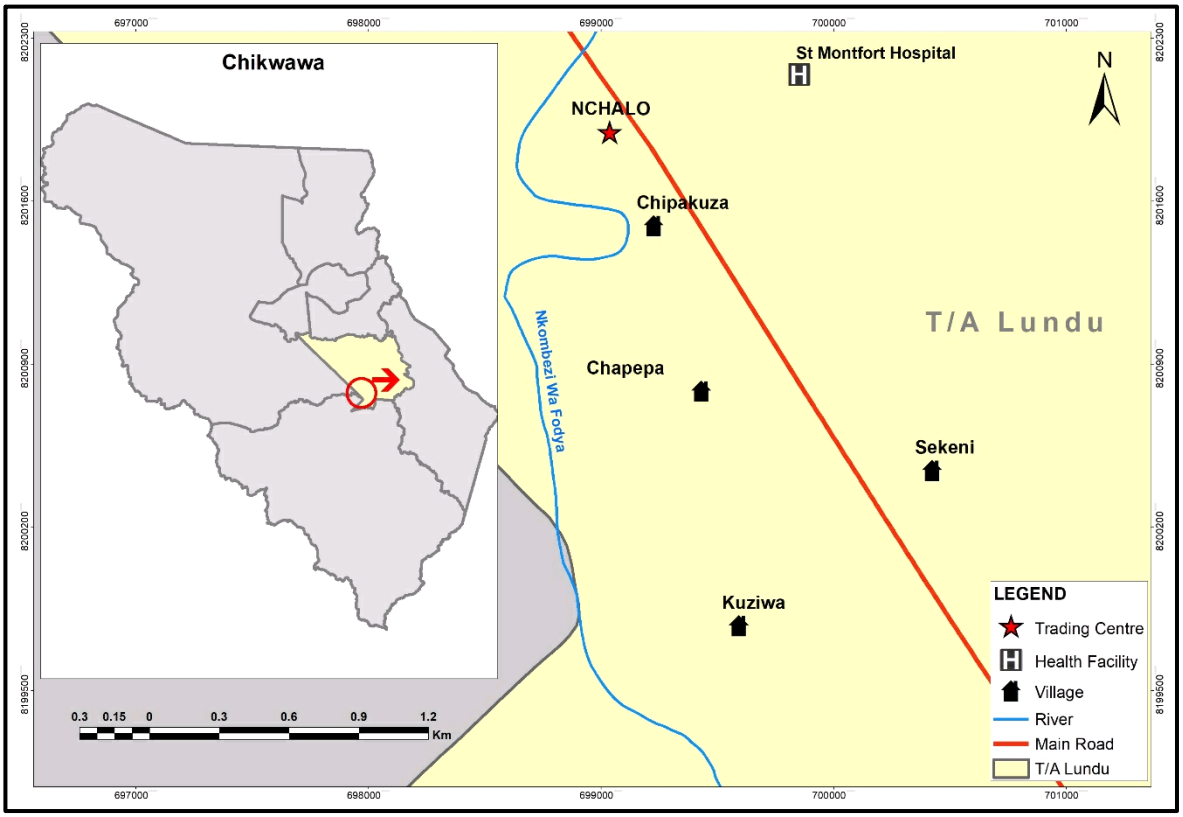


Figure 1: Map of study area Nchalo, T/A Lundu, Chikwawa.

Chikwawa is one of the districts within the Lower Shire valley of Malawi, and the studied area (Figure 1) is located in the middle part of the district (16°16'0" South and 34°55'0" East), particularly the villages around the famous Nchalo area in Traditional Authority of Lundu.

3.3. Geology and hydrogeology of the area

The geological formation of the Lower Shire Valley, with Chikwawa district inclusive as described by (Monjerezi, Vogt, Aagaard, & Saka, 2012), is greatly underlain by what is referred to as the Malawi Basement Complex (MBC). The MBC is composed of crystalline igneous to metamorphic rocks with high-grade charnockitic granulites and biotite-hornblende gneisses, and also marbles. This geological formation is overlain by the sedimentary rocks that originate from the Karoo super-group. Sedimentary rocks of the Karoo system found in the area include; coal shales, lower and upper sandstones, Mwanza grits and shales, as well as red beds (Sehatzdeh, 2011). Cretaceous Lupata formation, which consists of sandstone, shale, and marls, in turn, unconformably overlay the Karoo sedimentary rocks (Monjerezi, Vogt, Aagaard, & Saka, 2011). The large part of the mentioned geological successions of the lower shire valley is covered by unconsolidated quaternary alluvium which is variable, interdigitating sequences of clays, silt, sands, and occasional gravels (Sehatzdeh, 2011), all of which have an alluvial origin. The lower shire region being situated within the EARS, the area is intensely faulted with major faults such as Mwanza, Panga, Telegraph, and Nkombedzi (Sehatzdeh, 2011; Monjerezi, Vogt, Aagaard, & Saka, 2012).

The hydrogeology of the lower shire valley as reported by previous researchers, the main aquifer units in the order of increasing importance as groundwater resources are (a) the weathered and/or fractured basement rocks; (b) the Karoo and Cretaceous sedimentary rocks; (c) weathered basalts; and (d) the unconsolidated alluvial deposits (Sehatzdeh, 2011; Monjerezi, Vogt, Aagaard, & Saka, 2012). In general, the piezometric contours indicate a regime of groundwater flow towards the central axis of the valley i.e. towards the Shire River (Sehatzdeh, 2011).

3.4. Type of aquifer found in the study area

The investigation of the studied area consists of an unconsolidated type of aquifer (Figure 2). This aquifer is considered the youngest in Malawi, composing of alluvial and colluvial lithologies, and often lying unconformably on top of other lithologies (Fraser C. M., Kalin, Kanjaye, & Uka, 2020). These Quaternary alluvial deposits are mainly composed of clays, silts, sands, and gravels deposited in the floor of the East African Rift system (EARs) rift valley and along river plains (Fraser, Kalin, Kanjaye, & Uka, 2020). The lithologies of the deposits are highly variable (heterogeneous and anisotropic), and their composition tends to change considerably over short distances due to the nature of their deposition. The mineral assemblages of these alluvia suggest that they are derived from the Precambrian Basement Complex, primarily from the gneiss (Fraser, Kalin, Kanjaye, & Uka, 2020). This aquifer is relatively high-yielding in comparison with basement complex aquifers.

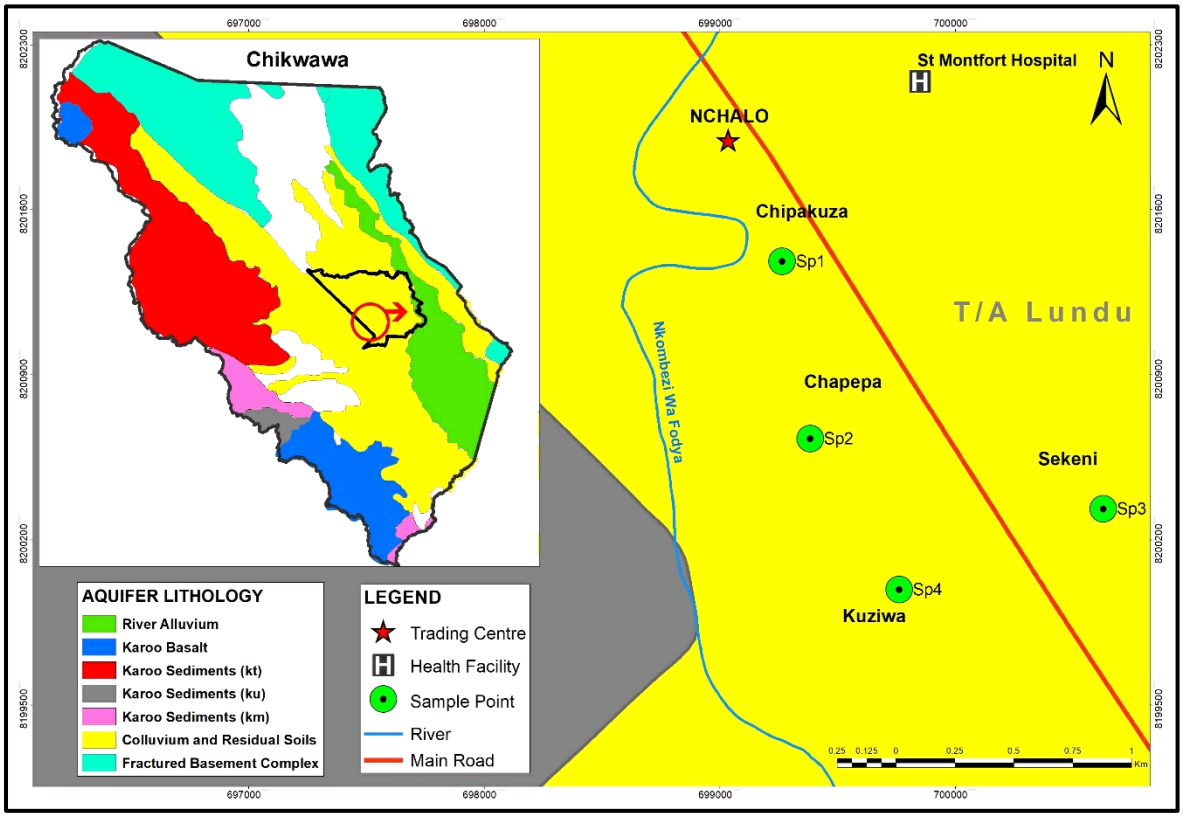


Figure 2: Map showing aquifers' lithology and sample points of the study area

3.5. Materials and Methods

Using quantitative techniques, a total of 8 groundwater samples from 4 boreholes were collected. These samples were collected from 4 different sites and their locations were selected randomly from areas that were near or around Nchalo. GPS was used to pinpoint the exact location of the sampled boreholes in the study area.

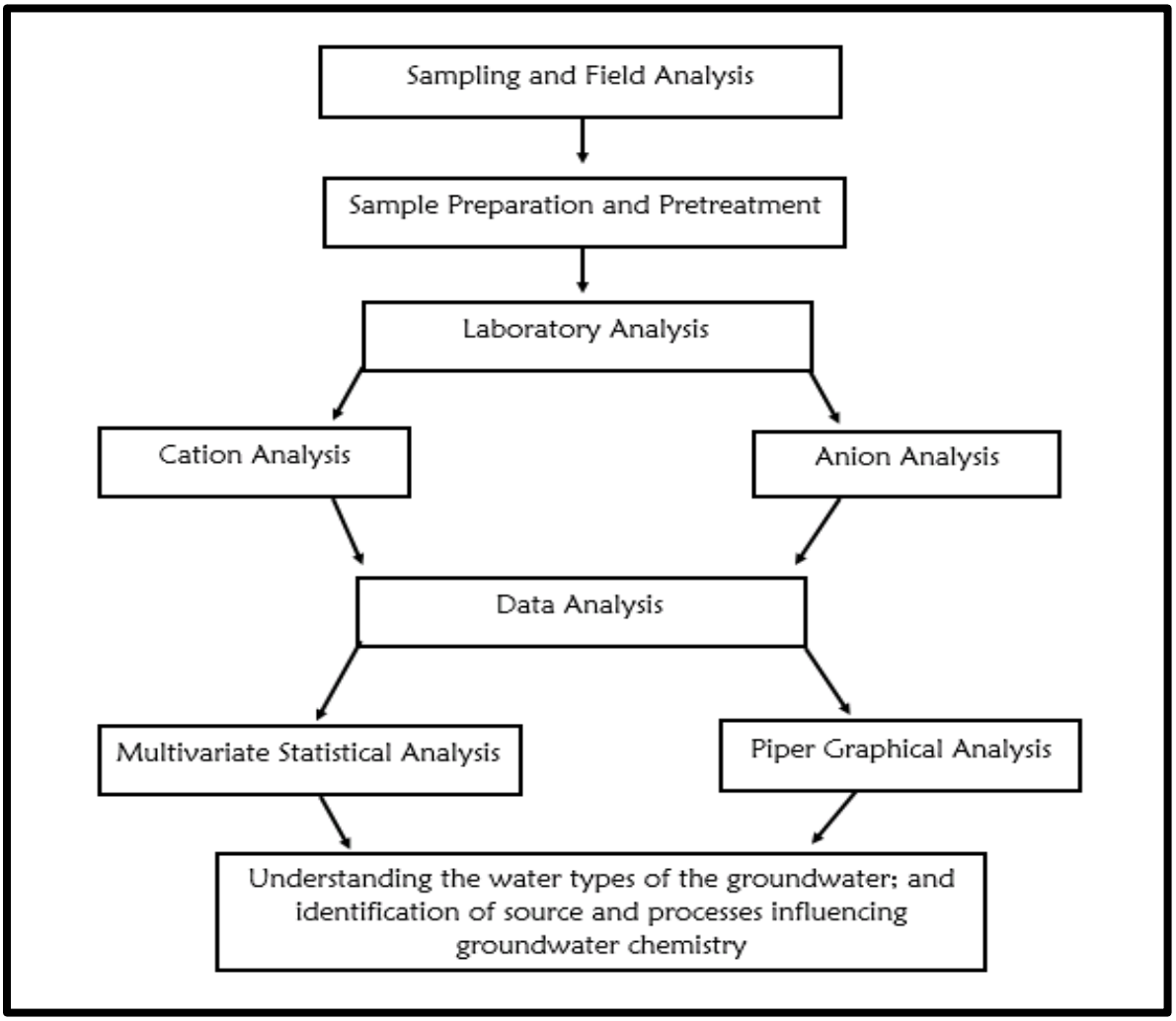


Figure 3: Methodology flowchart of this study

3.5.1. Fieldwork

At each sampling site, preliminary in-situ measurements of temperature, pH value, electrical conductivity, and total dissolved solids were performed using a multiprobe Hanna instrument model HI991300. To achieve this, the groundwater sample was first collected in a bucket and then the multiprobe meter was connected and its probe was immersed into the bucket. Readings were recorded after 10seconds had elapsed. Thereafter, the multiprobe meter was removed from the bucket and carefully dried with tissue paper. Then it was unconnected and placed back in its place till the next sampling site. Calibration of the instrument was done before each measurement as prescribed by the user manual.

At each site, two parallel samples were collected carefully in 125ml HDPE bottles, of which one of them was acidified with 1% hydrochloric acid (HCl), just after collection, to a pH less than 2.0 to fix the metals. The bottles were labeled with unique identification numbers using a permanent marker. Then the samples were stored in a cooler box to protect them during transportation. The groundwater samples were collected using the standard sampling procedure of the American Public Health Association (APHA, 2005). The samples were then sent Blantyre Water Department laboratory for water analysis.

3.5.2. Laboratory Analyses

At the lab, the samples were filtered through 0.45µm membrane filters and later on stored at 4^{o}C before chemical analysis. The acidified sample was transferred into 2 unused HDPE bottles for major cations and heavy metal including sodium (Na^{+}), potassium (K^{+}), magnesium (Mg^{2+}), calcium (Ca^{2+}), and iron (Fe^{2+}) analyses using UV/VIS Spectrophotometer, to determine the concentration of each element in the sampled groundwater.

The un-acidified sample was transferred into 125ml unused HDPE bottles for analyses of major anions. The concentrations of sulfate, nitrate, and phosphate were determined according to the respective specified methods: sulfate (SulfaVer 4 method) with SulfaVer 4 reagents, nitrate using HydroTest (HT1000), and phosphate (ascorbic acid

method) with PhosVer 3 powder pillow. Bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) were determine

3.5.3. Statistical Analyses

The quantitative data generated and presented in table form was analyzed using descriptive statistics such as mean and standard deviation of the variables, and multivariate statistical analysis techniques using PAST were also performed. The multivariate statistical analysis methods involved; Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA). Moreover, to understand groundwater-chemistry composition for the boreholes, the analyzed groundwater samples were plotted on the trilinear diagram using GW_Chart software.

3.5.3.1. Principal Component Analysis

Principal Component Analysis (PCA) is mostly applied to extract or identify the main factors that control the groundwater chemistry of each aquifer type and reduce the secondary factors. It also tries to explain the pattern of correlation within a set of observed variables (Sidibe, Lin, & Kone, 2019; Nagaraju, Thejaswi, & Sreedhar, 2016). The first principal component gives as many details as possible of the total explained variance of the variables. The second principal component clarifies as many details as possible of the remaining total explained variance of the variables, and so on. The PCA was done using PAST software.

3.5.3.2. Hierarchical Cluster Analysis

Liu, et al., (2019) and Chai, Xiao, Li, & Liang (2020), defines Hierarchical Cluster Analysis (HCA) as a statistical approach that is used for grouping the sampled groundwater sites by aquifer type, clustering them together, and studying the hydrochemical parameters according to their origins (Sidibe, Lin, & Kone, 2019). The results obtained are usually displayed in a dendrogram of distance that is considered the best method to display the hierarchical cluster analysis results.

3.5.3.3. Piper Diagram Analysis

Piper diagram analysis, also called trilinear diagrams (Figure 4), is a combination of plotted proportions (in meq/L or mg/L) of anion and cation triangles that lie on a

common baseline (Saveca, 2016). The piper diagram shows the similarities and differences among

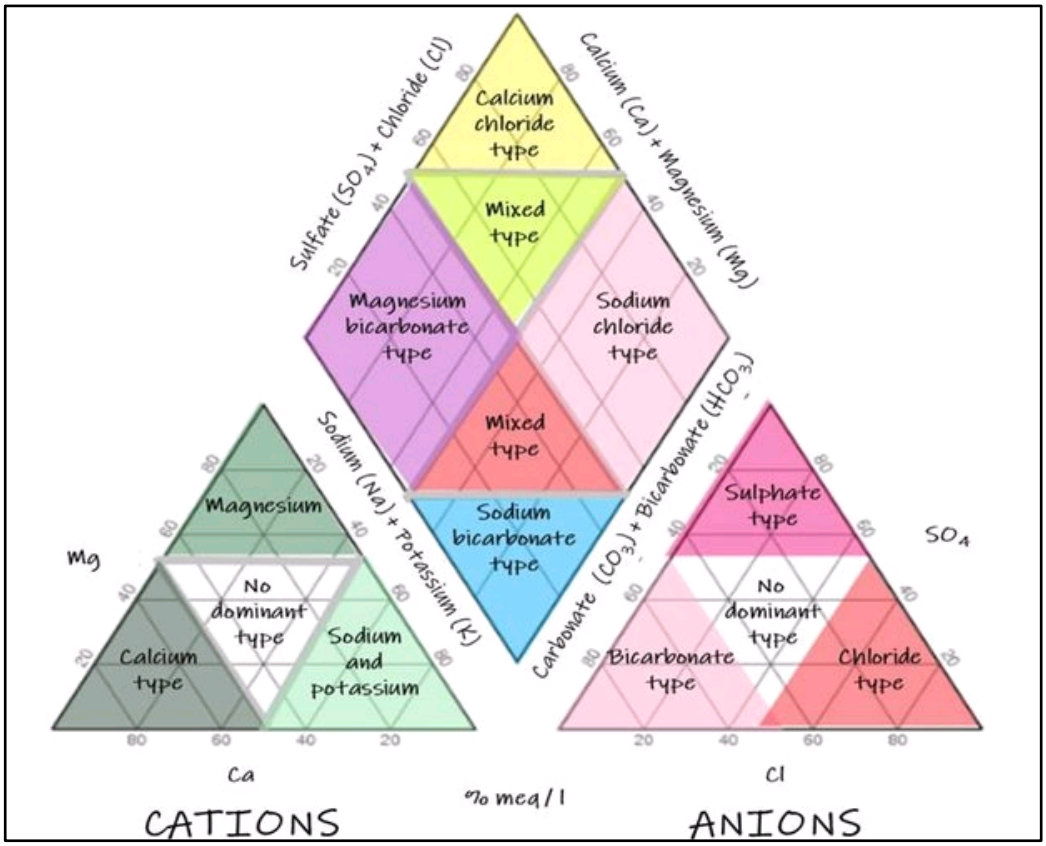


Figure 4: Piper diagram template (Abreha, 2014)

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1. Groundwater Chemistry

The results of chemical analyses and field measurements for 4 groundwater samples are summarized in Table 1. The water samples had average temperatures during sampling of around 27.35^{o}C, reflecting the average groundwater temperature of the sample sites. The pH values of the studied samples varied from 7.48 to 8.05, which is within the permissible ranging 6.5 to 8.5 of WHO (2008) and the median value was 7.81. Electrical Conductivity (EC) of the studied groundwater samples varied considerably from 1013 to 1889 µS/cm, and correspondingly TDS ranged from 508 to 945 mg/l. Based on the EC, the groundwater of the studied areas or sites are slightly saline or brackish (>1000 µS/cm).

Table 1: Summary of descriptive statistics of different field and hydrochemical parameters of all the 5 groundwater samples (all units are in mg/l, except for EC (µS/cm), Temperature (^{o}C), and pH)

Parameter	Minimum	Maximum	Median	Mean	Standard Deviation
pH	7.48	8.05	7.81	7.7875	0.1285415
Temp	26.1	28.2	27.35	27.25	0.9110434
EC	1013	1889	1465	1458	390.8887
TDS	508	945	732.5	729.5	195.7251
Ca	76	108	94	93	13.21615
Na	16	72	31	37.5	24.7319
Mg	22	36	31	30	6.324555
K	0.4	1.2	0.95	0.875	0.340343
Cl	12.8	64	30	34.2	21.5196
SO4	28	64	52.5	49.25	15.43535
HCO3	164.70	222.89	175.68	184.7375	12.7816

The mean abundance of major cations is $Ca^{+2} > Na^{+} > Mg^{+2} > K^{+}$, whereas the major anions is $HCO_3^{-} > SO_4^{-2} > Cl^{-}$. Among the cations, Ca^{+2} is the dominant and K^{+} is the lowest constituents, whereas HCO_3^{-} is the most abundant and Cl^{-} are the minor constituents in anions

Table 2: Water Quality Standards

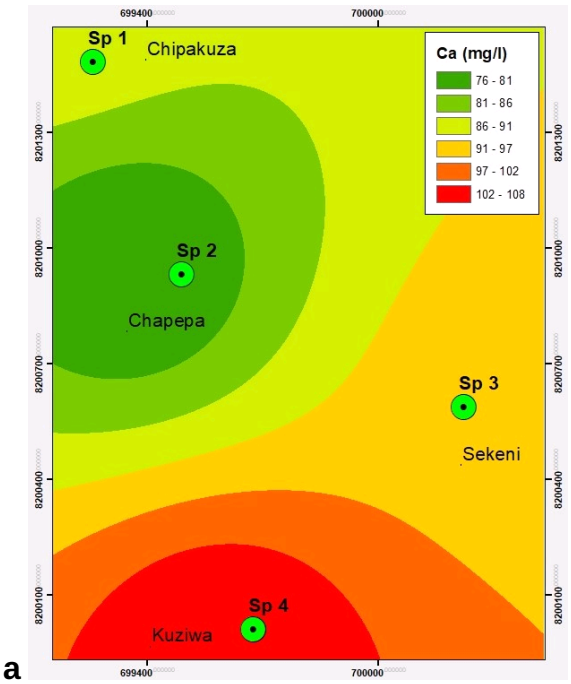
Constituents	Unit	Malawi Bureau of Standards (2005)	World Health Organization (2008)
Calcium	mg/l	250	200
Chloride	mg/l	750	600
Magnesium	mg/l	200	150
TDS	mg/l	2000	1000
pH		6.5-8.5	6.5-8.5
Sulphate	mg/l	800	400
Sodium	mg/l	500	200

Calcium (Ca) is the most abundant cation in the studied groundwater samples. Calcium concentration in groundwater varies from 76 to 108 mg/l. The maximum concentration of calcium is 108mg/l, reported in SP 4, a sample point in Kuziwa village. All of the groundwater samples were within the permissible limit of calcium for WHO (2008) and MBS (2005). According to Monjerezi (2012), and Kumar (2013), the basic sources of calcium in the groundwater resources are probably due to the dissolution of carbonate rocks, such as calcite and dolomite, which may be found in the area; and the weathering of amphibole and pyroxene derived from the sediments and sub extensions of the Basement Complex in the area. Another study also agreed that indeed the chemical breakdown of calcic-plagioclase feldspars and pyroxenes may be responsible for calcium in the groundwater (Saha, Selim Reza, & Roy, 2019).

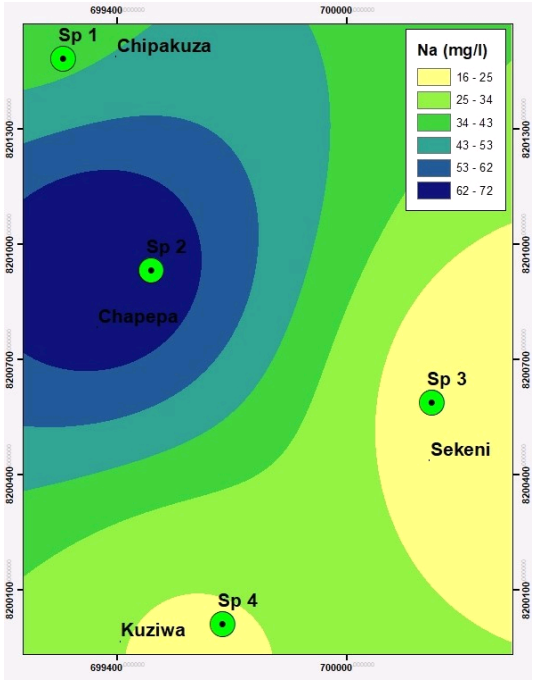
Sodium (Na^{+}) is the most abundant member of the alkali metal group of studied

groundwater. The sodium concentration of the sampled groundwater varies from 16 to 72 mg/l. The

Magnesium in the sampled groundwater resources may be derived from the decomposition of mafic or ferromagnesian minerals like olivine, pyroxene, amphiboles, and dark-colored micas which are constituents of the aquifer in the study area (Monjerezi, Vogt, Aagaard, & Saka, 2012; Chai, Changlai, Li, & Liang, 2020), and also from the dissolution of carbonate rocks such as dolomite (Kumar, 2013). The maximum amount of magnesium is found in the groundwater at SP 4 (Kuziwa village) is 36 mg/L, and the minimum concentration is reported in the groundwater at SP 2 (Chapepa) 22 mg/L. The average concentration of potassium (K^+) in the study is 0.82/mg/L, whereas the maximum content of K^+ is 1.2 mg/L at SP 3 (Sekeni) and the minimum concentration is 0.4 mg/L at SP 2 (Chapepa). Potassium may have resulted from the chemical decomposition of the silicates especially clay minerals (Saha, Selim Reza, & Roy, 2019), which may be derived from the superficial deposits. The low levels of K in the groundwater may be due to the consequences of its tendency to be retained in clay minerals and to contribute to the formation of secondary minerals (Gebretsadik, 2010).



a



b

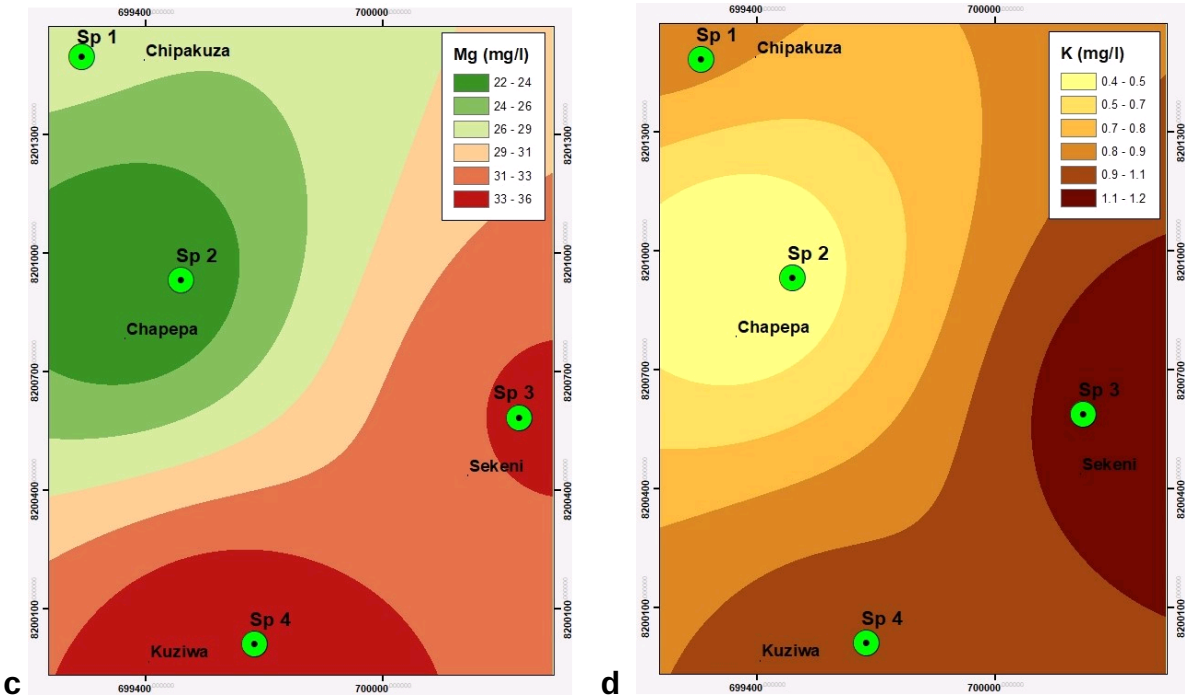
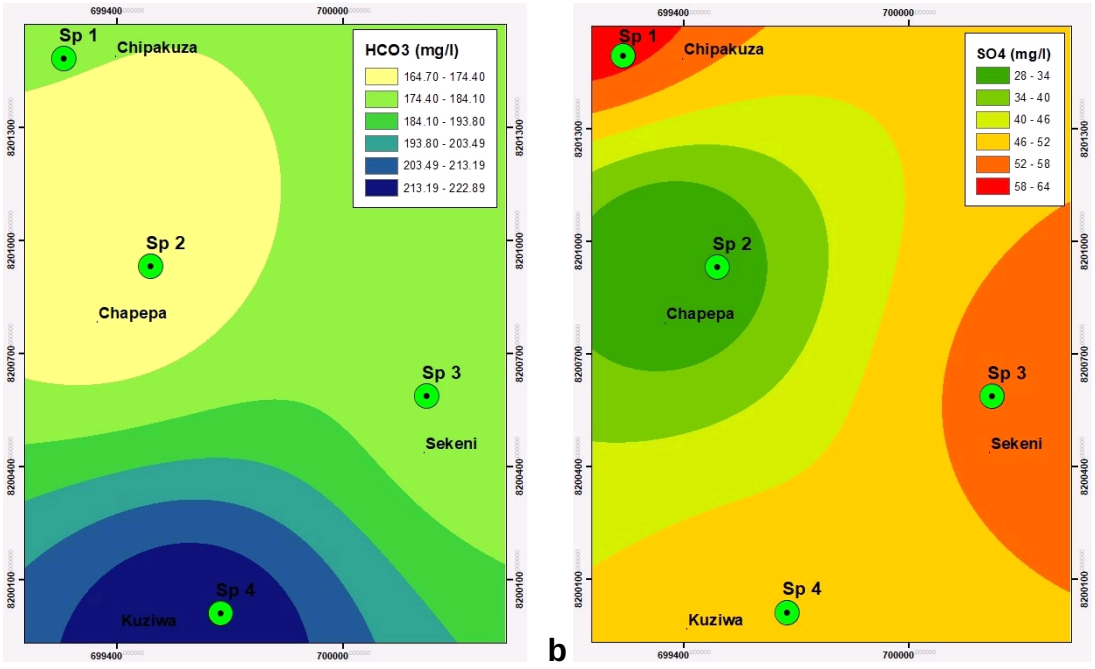


Figure 5: Spatial distribution of cations (a) Calcium, Ca; (b) Sodium, Na; (c) Magnesium, Mg; and (d) Potassium, K. Surface maps created using the Inverse Distance Weighted (IDW) method in ArcGIS 10.5. More features are detailed in Figures 1 and 2

Bicarbonate ions may have resulted from the weathering of silicate minerals, these results are consistent with what Monjerezi (2012) found, that the dissolution of feldspars and ferromagnesian minerals by H_2CO_3 charged water leads to the production of bicarbonates. The concentration of bicarbonate in the studied samples varies from 164.7 mg/l at Chapepa (SP 2) to 222.89 mg/l at Kuziwa (SP 4). The occurrence of sulfate in groundwater may have resulted from oxidation of sulfur in the igneous rocks, and the dissolution of the other sulfur-bearing minerals i.e. gypsum (Gebretsadik, 2010)

. Sedimentary rocks, such as shale, may also play a key role in this connection by the oxidation of

The chloride (Cl) concentration of groundwater may be attributed to the presence of chlorides from rocks, and evaporite minerals. The mean amount of chloride in the studied samples is 30.96mg/l. The chloride contents of the sampled groundwater range from 12.8 to 64 mg/l. The low value of chloride ions is probably an indication of the low salinity of the sampled sites. As indicated by (Monjerezi, Vogt, Aagaard, & Saka, 2012; Missi, 2018), the increase in chlorine concentration may be attributable to mixing with high salinity groundwater followed by mineralized seep from sedimentary Karoo and Cretaceous Lupata sediments. As such, a high concentration of chloride found in the boreholes of Sekeni (SP 3) and Chapepa (SP 2) villages that could be resulted from the mixing of freshwater with saline groundwater.



c

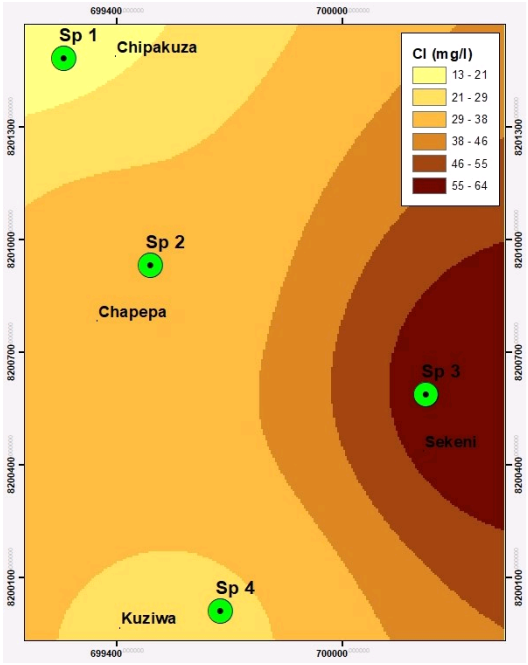


Figure 6: Spatial distribution of anions (a) Bicarbonate, HCO_3 (b) Sulphate, SO_4 and (c) Chloride, Cl

4.2. Multivariate Statistical Analyses

To understand the different associations between the main hydrochemical variables, a Pearson correlation matrix (**Table 3**) was establishes to determine the relationships between the different variables or chemical descriptors. This matrix shows a strong positive correlation between pH, TDS, and EC; Mg, Ca, and K; Cl and pH; K and SO_4; Mg, HCO_3 and Ca. A moderate uphill (positive) relationship is observed between Cl, EC, and TDS. The correlation between Mg, Ca and HCO_3 could indicate that they originate from the same source such as the dissolution of carbonate rocks such as calcite and dolomite (Kumar, 2013).

Table 3: Correlation matrix for all groundwater samples (n=4)

Variables	pH	EC	TDS	Ca	Na	Mg	K	Cl	SO4	HCO3
Ph	1									
EC	0.741	1								
TDS	0.746	1.000	1							
Ca	-0.619	-0.585	-0.589	1						
Na	0.195	0.443	0.443	-0.871	1					
Mg	-0.369	-0.388	-0.390	0.957	-0.946	1				
K	-0.108	-0.436	-0.435	0.808	-0.992	0.898	1			
Cl	0.705	0.622	0.624	0.065	-0.403	0.349	0.429	1		
SO4	-0.250	-0.791	-0.788	0.593	-0.757	0.567	0.801	-0.066	1	
HCO3	-0.809	-0.444	-0.451	0.869	-0.528	0.754	0.419	-0.160	0.184	1

4.2.1. Principal Component Analysis

The PCA was performed out on a data matrix consisting of 4 points representing prospected samples, and the 7 chemical variables measured or analyzed during laboratory analysis. Only the principal components with eigenvalues>1 are used to extract the main components (Chai, Changlai, Li, & Liang, 2020). Table 4 summarizes the PCA results, including the loadings, eigenvalues, and variance elucidated by each principal component (PCs). Principal components 1, 2, and 3 accounted for 68.37%, 18.60%, and 13.03% respectively of the variance. Two PCs with eigenvalues >1 explaining 86.97% of the total explained variance of the dataset. As a result, the total variance of PCA was obtained by the first two PC which has eigenvalus>1 explaining

86.97% of the total explained variance, and these are shown on the scatter plot represented in figu

Table 4: Loadings for the principal components and the variables

	PC 1 (68.37%)	**PC 2 (18.60%)**	**PC 3 (13.03%)**
Ca	0.94979	-0.28808	0.1221
Na	-0.98091	-0.18303	0.065686
Mg	0.9795	-0.0076301	0.20131
K	0.95122	0.26583	-0.15657
SO_4	0.72116	0.025231	-0.69231
Cl	0.27724	0.86592	0.41631
HCO_3	0.67856	-0.60359	0.41862
Eigenvalue	4.7859	1.30199	0.912112
%Variance	68.37	18.60	13.03
Cumulative %Variance	68.37	86.97	100.00

The results from the principal component analysis, the loadings, are significantly similar to the outcomes of the correlation analysis (Table 3). The scatter plot of PCA loadings scores for the dataset of groundwater samples (figure 7) shows the clustering of the sampled groundwater resources in space and their spatial distribution. From the figure, it is possible to understand the relations between the measured elements. Principal component 1 (68.37%) of the variance mainly describes samples with a higher concentration of Ca, Mg, K, SO4, and HCO3. The concentration of the well correlated Ca, Mg and HCO3 in PC 1 may indicate the dissolution of aluminosilicate and carbonate rocks, which may originate from the Cretaceous and Karoo sedimentary rocks and their derived colluviums. The first PC includes boreholes coded SP-1 and SP-4. The second principal component (18.60%) illustrates samples with high chloride concentration as indicated in Table 4 of the loadings scores, and this includes sampled groundwater from boreholes coded SP-3. The chloride concentration may indicate the weathering of evaporate minerals like halite.

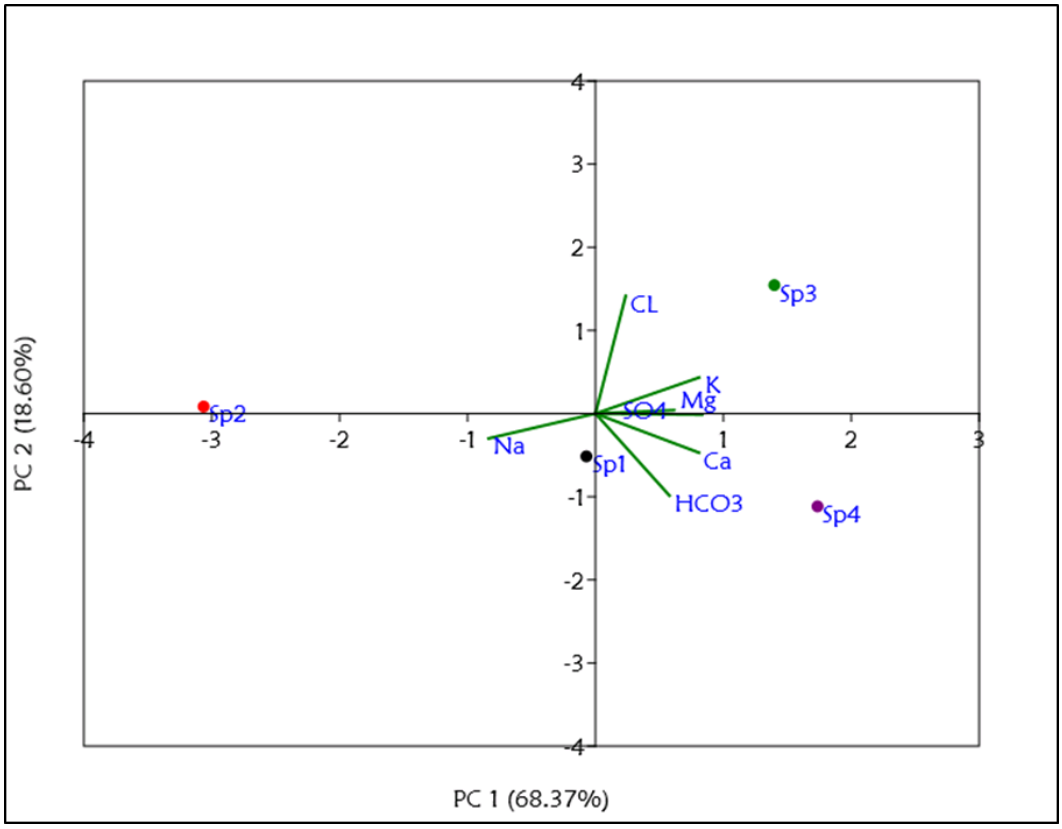


Figure 7: Scatter plot for the first two principal components explaining 86.97% of the hydrogeochemistry information

4.2.2. Hierarchical Cluster Analysis (HCA)

Hierarchy cluster analysis (HCA) demonstrated meaningful results in previous studies (Monjerezi, Vogt, Aagaard, & Saka, 2011). This study's approach was to select major chemical variables and use them in an HCA utilizing Ward's linkage rule, and construct a dendrogram (Figure 8). Ward's linkage rule indicates that the shorter the distance between two data points on a dendrogram, the greater the similarity between them (Wu, Chen, & Zhang, 2015; Liu, et al., 2019). As such, the waters of the same class

have a small connection distance between them according to their resemblance.

The cluster analysis of variables defined three classes: the first in red color (Ca, HCO3 and SO4) indicates the important calcite weathering processes that are also related to gypsum weathering processes; the second in blue color (Mg, K, and Cl) suggests evaporite weathering (possibly halite and sylvite), and also the weathering of aluminosilicate minerals; the third class in green color (Na) probably indicates the dissolution of $NaHCO_3$, and also the cation-exchange reactions between Na and Ca+Mg on authigenic clay silicates (Gebretsadik, 2010; Monjerezi, Vogt, Aagaard, & Saka, 2012).

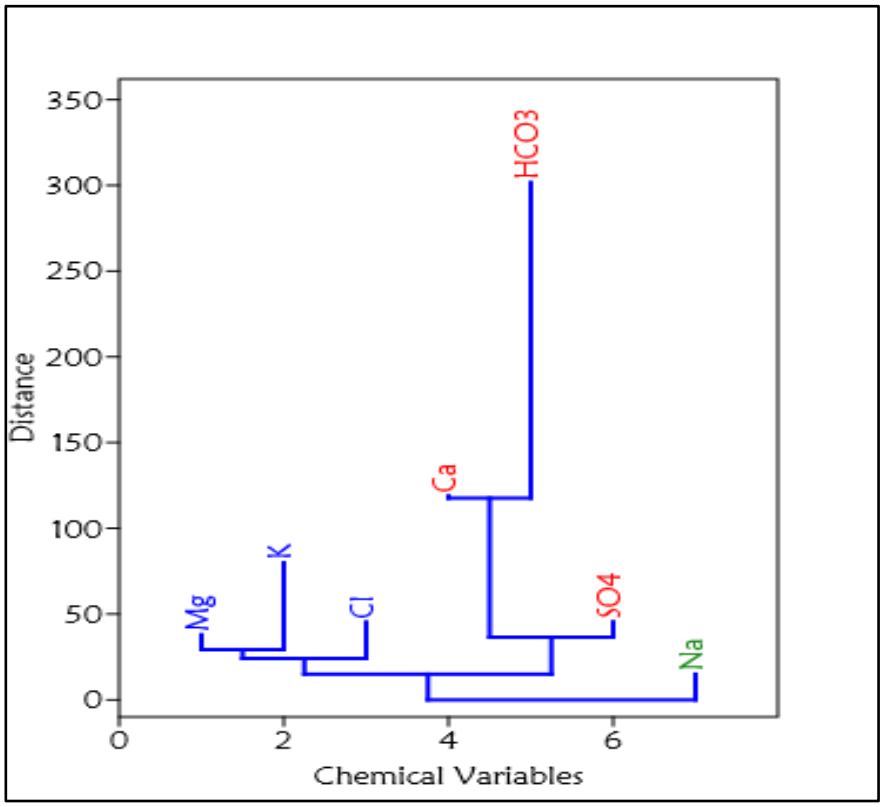


Figure 8: Dendrogram for the groundwater samples based on similarities among the major chemica

In this study, the grouping into three clusters of the sampled groundwater resource gave satisfactory results at forming geochemical distinct clusters. The produced clusters (Figure 9) are distributed as follows: groundwaters from Chipakuza (SP 1) and Kuziwa (SP 4) compose cluster 1; those from Sekeni (SP 3) compose cluster 2; and Chapepa (SP 2) cluster 3. There is a significant correlation between the two clusters (C1 and C2), which has seen their similarity in the dendrogram (Figure 9) and the samples from these clusters have relatively lower saline levels. The sample in C3 is rather different from the other as it has a relatively high brackish water as indicated by the EC value 1889 µs/cm (Appendix 2) and high values of sodium.

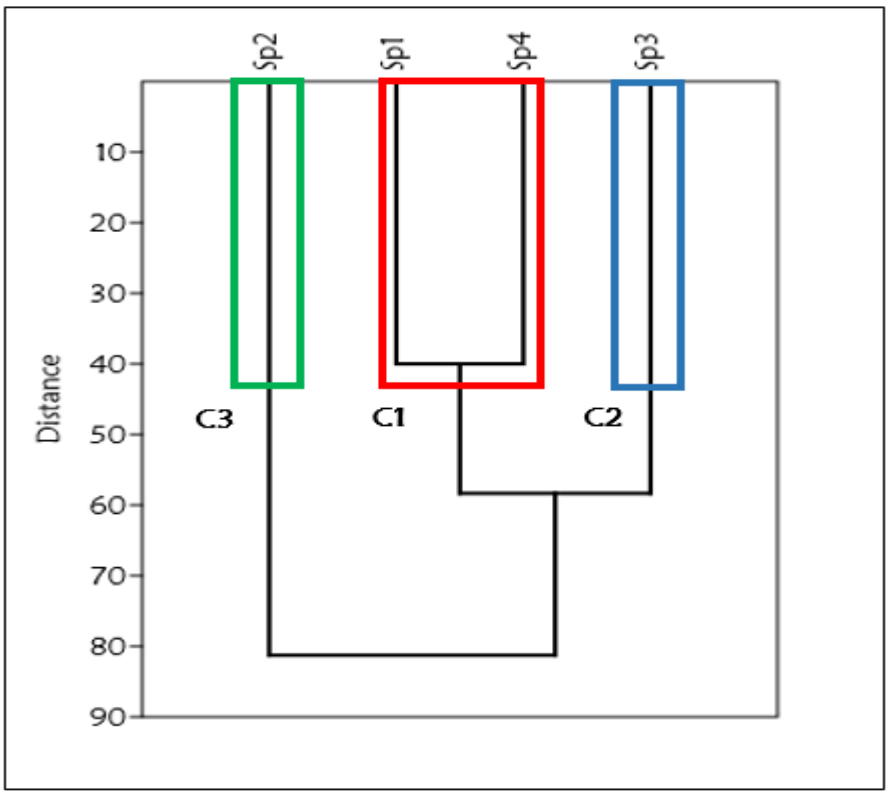


Figure 9: Dendrogram for the sampled groundwater resource sites

The results obtained from principal component analysis (PCA) and hierarchy cluster analysis (HCA) correspond well. The results correspond in the sense that cluster 1 (composed of SP-1 and SP4) both have considerably high positive PC1 values of Ca, Mg, K, SO4, and HCO3, and these values do vary. Cluster 2 (composed of SP-3) also corresponds positively with PC2 which correlates with chloride.

4.2.3. Piper Diagram Analysis

The piper diagram is an important means to comprehend the hydrochemical characteristics, hydrochemical types, and hydrochemical evolution in groundwater (Kumar, 2013; Zhang, et al., 2020). Figure 10 shows that the majority of the studied groundwater samples are characterized by Ca-HCO_3 hydrogeochemical facies, and only one sample had a mixed Ca-HCO_3-Cl type. The piper plot revealed that of all the groundwater samples, calcium is the dominant cation. However, in the case of anions, the samples are of bicarbonate type and chloride type. The average trend of cations and anions of the studied sample sites is as follows: $Ca^{+2} > Na^{+} > Mg^{+2} > K^{+}$ and $HCO_3^{-} > SO_4^{-2} > Cl^{-}$, respectively. This order of chemical variables is due to the lithologic composition of the study area.

The summary of groundwater hydrochemical types of the studied samples is as follows: (1) Ca-HCO_3 water type at SP-1 (Chipakuza), SP-4 (Kuziwa), and SP-2 (Chapepa) which may be strongly associated with the dissolution of calcareous sandstones, calcite, and gypsum; and (2) mixed Ca-HCO_3-Cl water type at SP-3 (Sekeni) could mean weathering of evaporate minerals (halite) and dissolution of carbonate rocks.

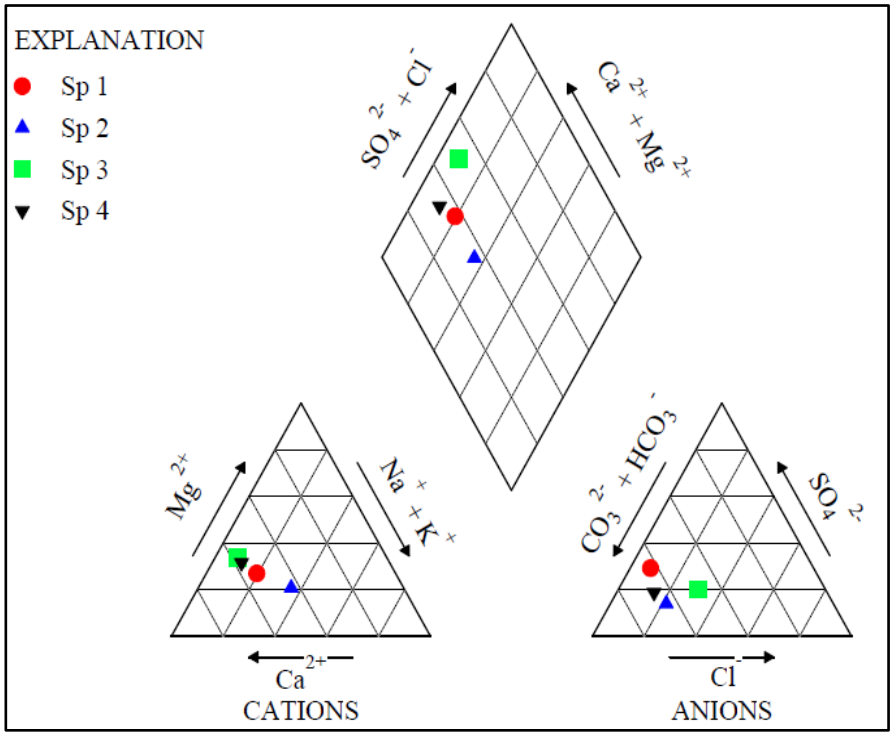


Figure 10: Piper Diagram of all groundwater samples

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The groundwater in the study area is slightly brackish or saline, with TDS ranging from 508 to 945 mg/l. The hierarchy cluster analysis (HCA) transformed the groundwater samples into three groups, and principal component analysis (PCA) identified that the

major chemical variables governing PC1 and PC2 were (Ca, Mg, K, SO_4, HCO_3) and Cl respectivel

5.2. Recommendations

- Constant monitoring of the water parameters in all the boreholes is required to take precautionary measures in case parameters changes to ensure that water in the study area meets the required standards for domestic use
- Determination of seasonal variations of hydrogeochemical parameters is also recommended.
- Investigation to identify other sources of chemical concentrates in groundwater

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APPENDICES

Appendix 1: Boreholes Location

Name of water point location	Borehole Code	GPS Coordinates
Chipakuza	SP 1	16°14.39761″S 34° 50.9234″E
Chapepa	SP 2	16°15.26612″S 34° 51.8492″E
Sekeni	SP 3	16°16.16858″S 34° 52.3739″E
Kuziwa	SP 4	16°19.02735″S 34° 51.9344″E

Appendix 2: Water quality test results of groundwater samples from selected borehole sites

ID	Temp	pH	TDS	EC	Na	Ca	Mg	K	Cl	SO4	HCO3
SP 1	29.2	7.68	508	1013	38	92	28	0.9	12.8	64	175.68
SP 2	32.8	7.94	945	1889	72	76	22	0.4	32	28	164.70
SP 3	34	8.05	831	1658	16	96	34	1.2	64	56	175.68
SP 4	31.5	7.48	634	1272	24	108	36	1	28	49	222.89