Hydro-chemical Evolution of Groundwater in Modjo River Basin, Central Ethiopia, Using Conventional and Multivariate Techniques

Didha Diriba Chali

A Thesis Submitted to Department of Applied Geology

School of Applied Natural Science

Office of Graduate Studies

Adama Science and Technology University

March, 2025

Adama, Ethiopia

Hydro-chemical Evolution of Groundwater in Modjo River Basin, Central Ethiopia, Using Conventional and Multivariate Techniques

Didha Diriba Chali

Advisor: Muhammad Haji (PhD)

A Thesis Submitted to Department of Applied Geology

School of Applied Natural Science

Presented in Partial Fulfillment of Requirement for Degree of Master's in Hydrogeology

Office of Graduate Studies

Adama Science and Technology University

March, 2025

Adama, Ethiopia

Declaration

I declare that this thesis proposal entitled "**Hydro-chemical Evolution of Groundwater in Modjo River Basin, Central Ethiopia, Using Conventional and Multivariate Techniques"** is my own work and has not been submitted to any university for similar purpose. The references used in this proposal are duly recognized by proper citations.

Didha Diriba ________________________ ________________

Signature Date

Recommendation

I, the major advisor of this thesis, hereby certify that I have closely advised the student while developing this thesis and read the draft thesis entitled "**Hydro-chemical Evolution of Groundwater in Modjo River Basin, Central Ethiopia, Using Conventional and Multivariate Techniques**" prepared under my guidance by **Didha Diriba**.

Therefore, I recommend the submission of the thesis to the department for further review and evaluation.

Muhammad Haji (PhD)	________________________	________________
Major Advisor	Signature	Date

Approval Page for thesis proposal

I/we hereby certify that the recommendation and suggestion given by the thesis review committee are appropriately incorporated into the final thesis entitled **"Hydro-chemical Evolution of Groundwater in Modjo River Basin, Central Ethiopia, Using Conventional and Multivariate Techniques**" by **Didha Diriba**.

Muhammad Haji (**PhD**) ______________________ _______________

Major Advisor Signature Date

We, the undersigned, members of the Board of Reviewers of the thesis open defense by **Didha Diriba** have read and evaluated the thesis entitled "**Hydro-chemical Evolution of Groundwater in Modjo River Basin, Central Ethiopia, Using Conventional and Multivariate Techniques**" and assessed the understanding of the candidate about the thesis. This is, therefore, to certify that the thesis is accepted and we recommend the implementation of the final version of the thesis.

______________________________ ______________________ ____________________

Chairperson Signature Date

______________________________ ______________________ ____________________

Reviewer 1 Signature Date

______________________________ ______________________ ____________________

Reviewer 2 Signature Date

Finally approval and acceptance of the thesis is contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

______________________________ ______________________ ____________________

Department Head Signature Date

______________________________ ______________________ ____________________

School Dean Signature Date

______________________________ ______________________ ____________________

Office of Postgraduate Studies, Dean Signature Date

Acknowledgment

First and foremost, I would like to express my heartfelt gratitude to my Almighty, whose unwavering guidance and supports have been the cornerstone of my journey. Dear God, your strengths have inspired me to overcome challenges and persevere in the face of adversity. Thank you for instilling in me the values of resilience, dedication, and integrity, which have shaped not only my academic pursuits but also my character.

Second, I extend my deepest appreciation to Muhammed Haji (PhD), my esteemed advisor, whose mentorship and insightful feedback significantly enhanced the quality of my work. Dr., your encouragement pushed me to think critically and develop my ideas further. Your support transformed my errors into meaningful lessons, shaping my growth as a researcher.

I am especially grateful to my brother, Engineer Balcha Tadesse, who has shown me that brotherhood transcends blood ties. Your unwavering support and motivation have been a source of inspiration throughout this journey. You have shown me that true brotherhood is born from friendship and support.

A special thanks to Tolesa Dabi **(**PhD**)** who supported me in various ways, from data analysis to providing constructive feedback during my career. Your collaborative spirit made a significant difference in my research experience. I truly appreciate your kindness and friendship.

I would also like to acknowledge my families for their unconditional love and understanding. Dear families, your support have been a strong foundation that enabled me to pursue my dreams.

I would like to sincerely thank Kegna School (Mr. Kaba and Mr. Wakshum) for giving me the time to learn. Time is more precious than anything, and I truly appreciate the opportunity to grow and gain knowledge."

Finally, I would like to thank the various offices and people that generously provided the necessary data for my research. Their contributions were crucial in shaping the outcomes of this study.

Table of Contents

List of figures

List of tables

List of Abbreviations and Acronyms

ASS	Atomic Absorption Spectroscopy
DEM	Digital Elevation Model
EC	Electric conductivity
GPS	Global positioning system
HCA	Principal component analysis
PCA	Hierarchical Cluster Analysis
PH	Power of hydrogen
SPSS	Statistical Package for the Social Sciences
TDS	Total dissolved solid
WHO	World Health Organization

Abstract

Groundwater is a vital resource in the Modjo River Basin of central Ethiopia, meeting the water demands for domestic, agricultural, and industrial uses. This study aimed to assess the hydro-chemical characteristics and evaluate the processes controlling the groundwater chemistry in the Modjo River Basin using conventional and multivariate techniques.

These water samples were collected from 79 groundwater points from different places and analyzed for major ions and physicochemical parameters in Engineering Corporation of Oromia (ECO). The result reveals that sodium ion is the dominant cations followed by calcium in the groundwater of the study area. NO_3^- *concentration ranges from 0.03 mg/L to 85.5 mg/L in all water samples, however, high amount of* NO_3^- *contents are observed in one deep well with a concentration of 85.5 mg/l(MM-9). The* F^- *concentrations varied from 0.07 to 1.9 mg/L in all water samples in the study area except for two deep wells that exceeds WHO standards. The results showed that the groundwater is predominantly of calcium-magnesium-bicarbonate type. Groundwater in the Modjo river catchments shows systematic hydro-chemical evolution from* $Ca\text{-}HCO_3$ *to* $Ca\text{-}Na\text{-}HCO_3$ *to* $Na\text{-}Ca\text{-}HCO_3$ *type water along the flow path from the upper part of the catchment to the lower part of the catchment. Interpretation of hydro-chemical data suggests that silicate hydrolysis and cations exchange are the major geochemical processes that control the hydrochemistry of the groundwater in the basin.*

With its integrated approach, this study provided valuable insights into the hydro-chemical evolution of groundwater in the Modjo River Basin, which can guide future groundwater development and management strategies.

Key words: volcanic aquifer, major ion, statistics, geochemical process, Modjo river basin, Ethiopia

CHAPTER ONE

INTRODUCTION

1.1. Background

Groundwater is an essential resource that sustains ecosystems, supports agricultural activities, and provides drinking water for billions of people worldwide (Gleeson et al., 2020; Hiscock, 2011; Hiscock et al., 2002; Wang et al., 2018). The demand for water rises along with the global population, which increases the world's dependency on groundwater resources(Vaux, 2011). Numerous factors, such as ion exchange, dissolution, precipitation of minerals through water rock interactions, various anthropogenic activities, geological structure, and other geochemical processes controlled the chemical composition of groundwater in the aquifer which resulted in different water facies (Belkhiri et al., 2010; Devaraj et al., 2020). One of the most fascinating and complex a phenomenon in water geochemistry is the chemical reaction between water and rock. Water's reaction to minerals and rocks determines the composition of both groundwater and surface water. Hence, the chemistry of water is an important factor determining its use for domestic, irrigation or industrial purposes. Despite its potential for variation, groundwater from different aquifers will continue to be exploited.

Groundwater from volcanic aquifer of Ethiopia serve as a major source of water for domestic uses, industries, recreation and livestock (Birhanu et al., 2021; Kebede, 2012; Mengistu et al., 2019). However, the potential of groundwater varies significantly owing to the complex geological condition of the volcanic rocks. Many volcanic rocks possess extremely heterogeneous structure and are chemically more reactive. This is due to the existence of fine particles and the abundance of vitreous matter; which results in complex flow and lithogenic contaminants in groundwater including F and As (Ayenew, 2005).

Studies on volcanic aquifers have been carried out in relation to the aspects of groundwater recharge (Demlie et al., 2007), origin and flow dynamics (Kebede et al., 2008; Mechal et al., 2017) water quality (Ayenew, 2008)geochemical evolution (Haji et al., 2021). Nevertheless, characterization of the groundwater flow system and geochemical evolution of volcanic aquifers is hydro-geologically challenging. This is mainly due to the heterogeneity and anisotropy of volcanic aquifers that resulted from the accumulation of lava and pyroclastic flows, the fracturing of volcanic rocks, different degrees of weathering, and the disruption of lithologies by tectonic (Kebede et al., 2008; Möller et al., 2016). Modjo River catchment that situated in the Ethiopian Rift Valley provides essential water for both agricultural and community uses (Alemu et al., 2022; Kawo & Karuppannan, 2018b; Negash et al., 2022; Wondimu Negash, 2021). The Ethiopian Rift System is a classic example of a continental rift where recent and active deformation, as well as volcanic activity, has occurred (Keranen & Klemperer, 2008). This resulted to the complex hydrogeological setting caused by the strong climate and physiographic difference, variability and lateral discontinuity of volcanic rocks, and the disruption of lithology by faults. In the present study, groundwater in a volcanic aquifer of Modjo River catchment that situated in the Upper Awash river basin, was investigated focusing on the hydro-chemical evolution of groundwater. The selected area represents the northwestern flank of the central main Ethiopian rift where geological formations, tectonic structures and relief features are highly complex and characterized by wide climate variation. The majority of the study area is composed of pyroclastic rocks and lacustrine sediment with primary porosity. The lacustrine deposit, Quaternary scoriaceous basalts, fractured ignimbrites, and fractured basalts make up the water bearing unit of the Modjo River Basin (Kawo & Karuppannan, 2018b). A sound understanding of the spatial variation of groundwater chemistry, its evolution and controlling mechanism is therefore required for an adequate development and management of groundwater resources in the basin.

Evaluations of groundwater hydrochemistry and multivariate techniques have been widely used to understand geochemical evolution of groundwater. Major ion chemistry helps to define chemical reactions, acquired by water–rock interaction, that control groundwater composition (Ahmed & Clark, 2016; Belkhiri et al., 2012a; Gastmans et al., 2016).

On the other hand, multivariate statistical method can reveal hidden patterns and relationships between various ions, assisting in identifying dominant processes and their spatial distribution, assisting in identifying geochemical controls on composition (Belkhiri et al., 2010, 2012b; Blake et al., 2016). Combining hydrochemistry and multivariate techniques allows for constraining geochemical evolution of groundwater and is also helpful to characterize groundwater quality.

Within this research attempt, the investigation of geochemical evolution of groundwater recharge is undertaken. This is achieved through the integration of geological, hydrogeological and hydro-chemical data. The approach employed in this study involves the conjunctive use of hydro-chemical data and multivariate statistical method. The main objective of this study was to investigate the geochemical evolution in the Modjo River catchment for an adequate development and management of groundwater resources in the basin.

1.2. Statement of problem

Studies on the hydro-chemical properties and geochemical evolution of groundwater are essential for groundwater planning and management. High-resolution groundwater prospect mapping availability is restricted to only a few localities of the Ethiopian Rift Valley (Bhowmick et al., 2023).

Understanding the hydro-chemical properties and geochemical evolution of groundwater is crucial for effective groundwater planning and management, especially in the context of increasing human activity and its impacts on the hydrologic cycle (Zhang et al., 2018). In Ethiopia, while the potential for groundwater resources is significant, it remains inadequately understood, particularly in the Modjo River Basin. Existing studies have limitations related to data availability, and spatial coverage, making it challenging to obtain a comprehensive understanding of groundwater chemistry in this region. Recent investigations have revealed a lack of detailed research focused on the geochemical evolution of groundwater in the Modjo River Basin (Desissa, 2016; Dula, 2010; Eshetu, 2021; Kawo & Karuppannan, 2018b; Olumana & Loiskandl, 2015). There is uncertainty gap with statistical nature of groundwater quality and the need for more refined assessments of hydro-chemical processes.

Therefore, there is an urgent need for a thorough investigation into the hydro-chemical evolution and interactions of groundwater in this area.

This study aims to assess the hydro-chemical evolution of groundwater in the Modjo River Basin using both conventional hydro-chemical methods and advanced multivariate statistical techniques. By integrating these approaches, the research will provide insights into the spatial variations in groundwater chemistry, identify underlying factors influencing water quality, and contribute to sustainable water management practices. The findings will address existing gaps in knowledge and offer new perspectives on the hydro-chemical processes that shape groundwater in the Modjo River Basin, ultimately supporting better groundwater resource management.

1.3 Research Questions

- What are the dominant hydro-chemical processes influencing groundwater chemical composition?
- What are the spatial distribution patterns of major ions in groundwater across the Modjo River Basin?

1.4. Objectives

1.4.1. General objectives

The general objective of the study is to examine geochemical evolution of groundwater in the Modjo River catchment.

1.4.2. Specific objectives

- To assess the chemistry of groundwater in Modjo River catchment
- To recognize and characterize the water types that exist in Modjo River catchment
- To investigate the spatial variations in groundwater chemistry within the Modjo River catchment.
- To evaluate the dominant hydro-chemical processes that control groundwater chemistry in Modjo River catchment.

1.5. Significance of the study

Ethiopia's groundwater resource potential is estimated to be approximately 40 billion cubic meters(Mengistu et al., 2019). Groundwater in Ethiopia is found in various locations throughout the country, primarily in aquifers that are associated with different geological formations. Hydro-chemical determination of groundwater is critical for several reasons. Since, there are several infrastructures that are under construction and have already been completed in and around the study area (Gada City) it requires hydro-chemical determination. It used to predict future impact of infrastructure on the water chemistry of the area. The presence of constructions can affect both quality and quantity of groundwater. As infrastructures develop, groundwater level decreases due to reduced infiltration of rainwater into ground. It often causes by increased impervious surfaces like concrete and asphalt. This can prevent water from reaching the aquifer and leading to less groundwater recharge and potential depletion over time. These infrastructures can also impact groundwater quality by altering the natural flow of water by creating pathways for pollutants to infiltrate the aquifer, or directly introducing contaminants through leaks or spills. So that, the study will contribute better understanding of the groundwater hydro-chemical processes in the Modjo River catchment. Moreover, it identifies the hydro-chemical processes that influence groundwater composition. Therefore, it is essential to carry out local scale monitoring and evaluation in order to analyze the hydro- chemical processes in order to have a better understanding of the chemistry inside these sorts of volcanic aquifers.

1.6. Limitation of the study

There is no research which completely free from limitation. Therefore, like other studies, the researcher has encountered some problems during the process of conducting this study. The potential limitations of this study include challenges related to data availability and quality, such as, insufficient temporal coverage to capture seasonal variability. Another limitation of the study is the lack of long-term monitoring data, which makes it challenging to assess the historical evolution of groundwater chemistry and the cumulative impact of natural processes and human activities over time. This limitation can hinder the ability to identify trends or predict future changes in groundwater quality and hydro-chemical dynamics, reducing the study's capacity for long-term planning and management recommendations.

Addressing these limitations requires robust data collection, advanced modeling techniques, and careful interpretation to ensure reliable and meaningful conclusions.

1.7. Description of the Study Area

1.7.1 Location and Accessibility

The Modjo river catchment is situated in the upper Awash River basin in the central Ethiopian Rift Valley. Geographically, it is situated in the northern hemisphere between latitudes 8°16′N and 9°18′N and longitudes 38°50′E and 39°17′E It covers an approximate an area of 1901.69 km^2.which represented about (1.72)% of the total area of Awash River Basin. The study area can be accessed by Addis Ababa-Modjo-Adama asphalt road, Hawasa-Addis Ababa asphalt road and others. Intra-basin areas can be accessed by numerous gravel and dry weather roads

The watershed's altitude varies from 1590 meters above sea level near the riverbed to 3091 meters above sea level in its upper portion.

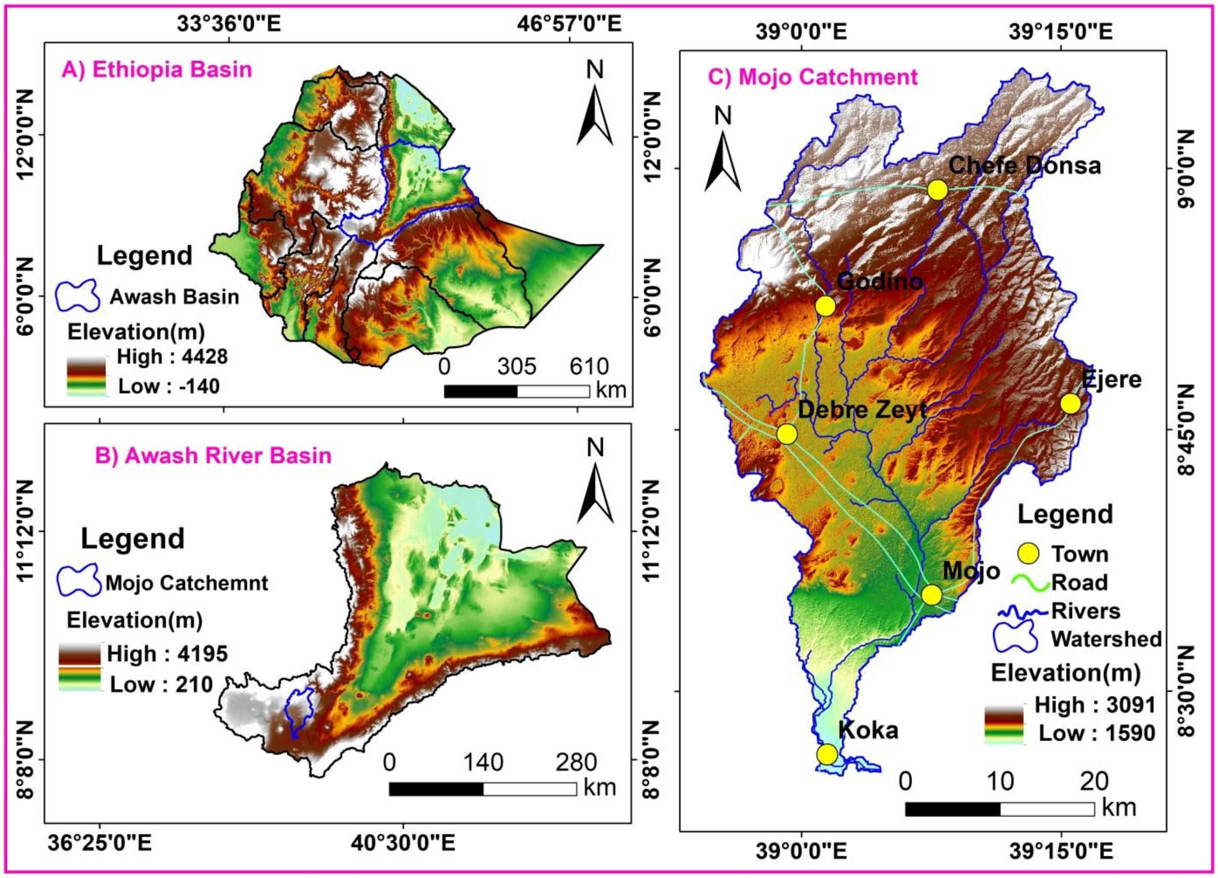


Figure 1: 1 Location map of the study area

1.7.2. Drainage Aspect of Study Area

1.7.2.1 Drainage

Modjo River basin is one of the Awash River's major tributaries. It runs through the basin, picking up water from several streams like Berka, Gumera, Selale and tributaries along the way. The Modjo River travels across the basin, collecting water from different streams and tributaries as it flows from the Ethiopian Highlands. The watershed empties into the Koka Reservoir, which is built on the Awash River, after draining into the perennial Modjo River (Mamo, 2002). The basin is made up of a series of smaller watersheds and catchment areas that contribute to the main drainage system (fig.1.2). The distribution and flow of water within the basin are influenced by these smaller watersheds and tributaries, which vary in size and shape.

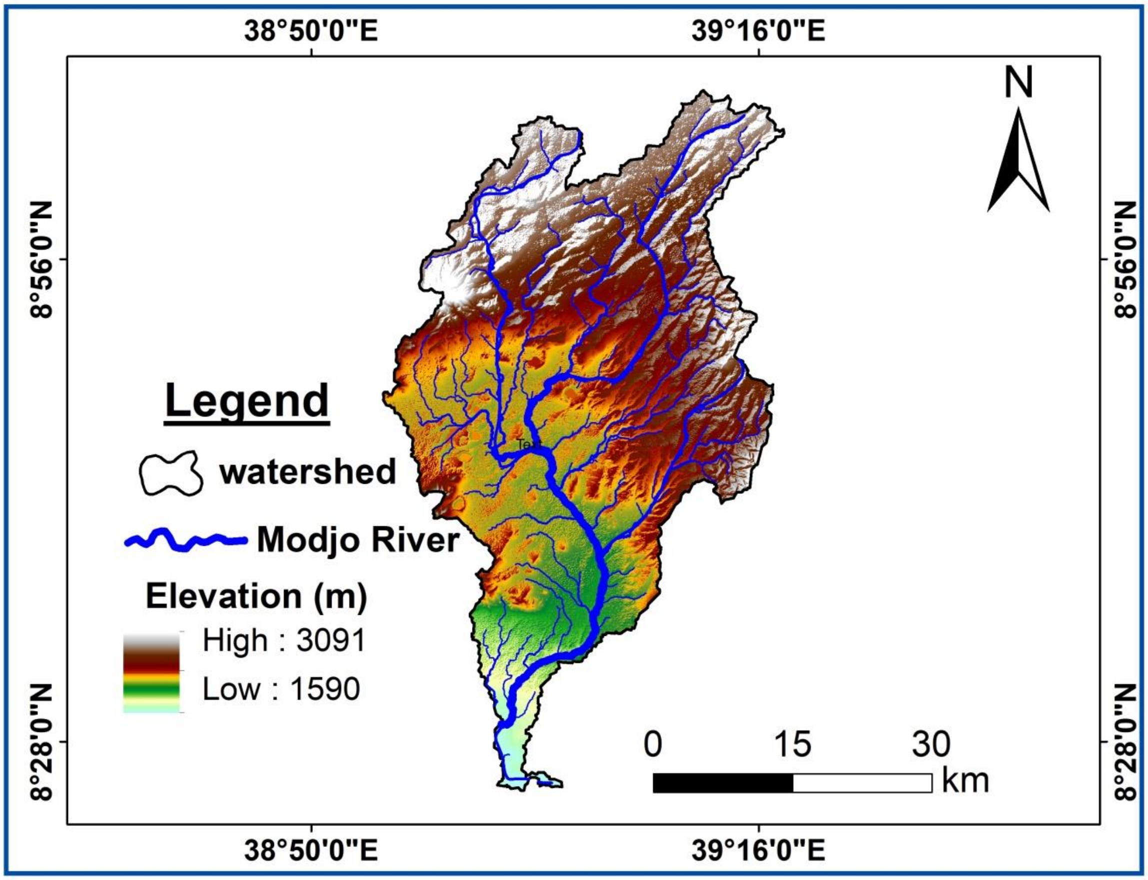


Figure 1: 2 Drainage of study area

1.7.2.2. Climate Characteristics of the Area

The Modjo River Basin's climate is impacted by its location within Ethiopia, which has a variety of climatic zones. The lower elevations of the basin, notably in the east and southeast, have a tropical wet climate. Throughout the year, this region receives rather significant levels of rainfall, with a peak during the summer months (June to September). On average, the catchment receives approximately 76.9 millimeters of rainfall annually (Appendix 1). Temperature in the catchment ranges from mild to hot. The mean daily temperature usually falls between 4°C and 11°C, and the average monthly temperature ranges from 11°C to 27°C (Appendix 2)

The research location is situated in the primary Ethiopian rift and primarily influenced by the southerly and easterly air currents from the Indian Ocean. Consequently, these air currents bring `rainfall that exhibits bimodal characteristics. According to data obtained from meteorological services agency, precipitation data from 5 stations in the area signify that there is high peak of rainfall from June to September, low from March to May and dry from October to February.

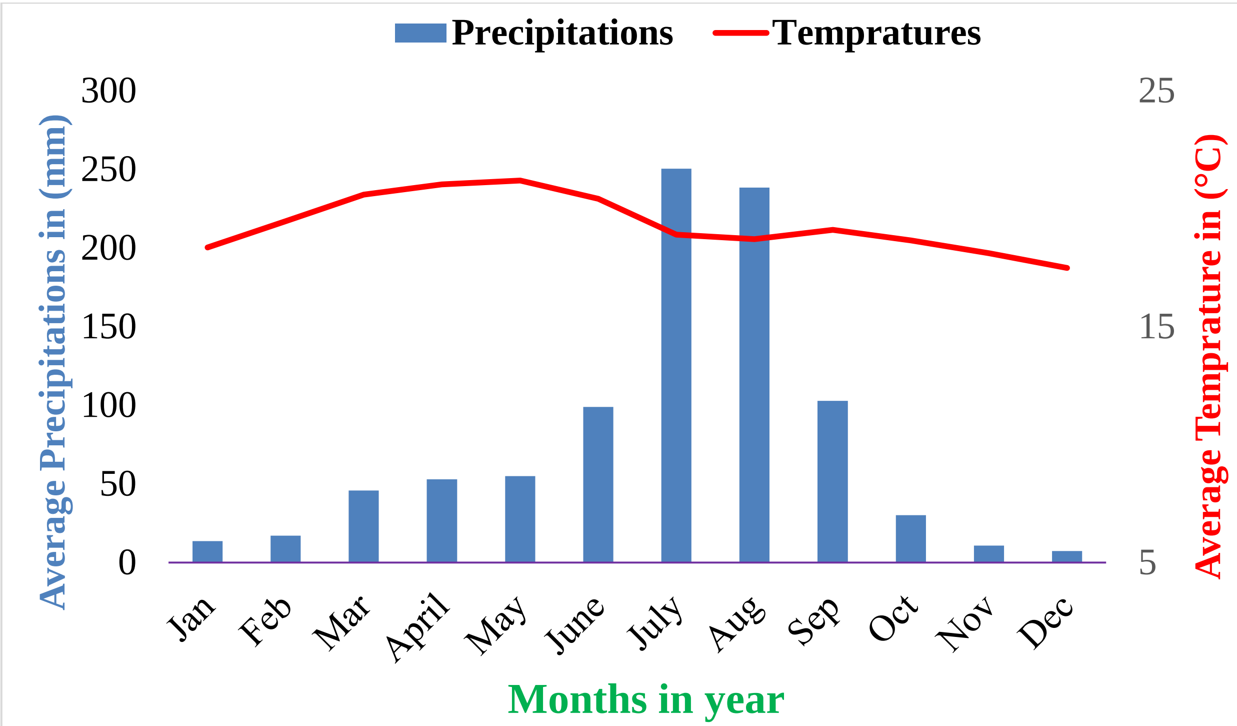


Figure 1: 3 Average monthly climate and rainfall of stations

CHAPTER TWO

LITERATURE REVIEW

2.1. Review of Hydro-Geochemical Processes and the Dynamics of Major Ions in Groundwater

The bulk of the main ions are deposited as total dissolved solids rise along the groundwater's flow path as it passes through the saturated zone. The two types of major ions are called anions and cations, respectively, depending on their charge. Because water must be electroneutral, both cations and anions are present in equal amounts. The four main cations found in groundwater are potassium (K), sodium (Na), magnesium (Mg), and calcium (Ca) (Huang & Ma, 2019).

Ca and Mg concentrations can be varying over a wide range in natural water due to geological influences, depending on the chemical history. Generally, Ca concentrations are somewhat greater than those of Mg in freshwaters because the Earth's crust contains greater Ca abundances. In oceanic and estuarine waters, on the other hand, Mg may often dominate Ca concentrations. Variations in cation abundances occur when exchange processes take place (Şen, 2014). Through the breakdown of minerals that react with carbon dioxide to generate carbonate minerals, calcium and magnesium are able to reach groundwater reservoirs (Ayub et al., 2020).

It is possible for Ca and Mg to exchange ions with sodium. The majorities of Na compounds dissolve easily and stay in solution most of the time. This is as a result of its absence from significant precipitation reactions. While Na and potassium have many similarities, they also differ greatly in a few key aspects that are related to their presence in water. Although rocks with high K abundances are usually resistant to weathering, Na is easily soluble in them. Since K also frequently adsorbs to the solid phase form new minerals throughout various processes, it is typically found in groundwater at smaller concentrations than other cations(Şen, 2014).

Quantities of anion can provide information on a variety of hydro-geochemical processes. The chloride (Cl) found in groundwater is produced when precipitation interacts with the geology of catchments and aquifers (Möller et al., 2016). Cl's conservative characteristics make it a useful indication of groundwater chemical reactions. Since Cl salts only precipitate in abundances greater than those of seawater, it tends to stay in solution. As a result, declining Cl concentrations can indicate the entry of freshwater into an aquifer. In contrast, a number of processes could lead to rising Cl concentrations. These could involve the breakdown of minerals containing chlorine and the blending of groundwater with salinity-rich fluids, including seawater intrusions(Şen, 2014).

Sulfate is typically present in groundwater at lower amounts than Cl. Both natural and man-made sources can be linked to the genesis of SO4 in groundwater. Naturally occurring processes that dissolve sulfur minerals and oxidize sulfide minerals can release SO4. On the other hand, low SO4 concentrations are a feature of igneous and metamorphic rocks, which means that groundwater found in these rocks is probably also low in SO4(Sharma & Kumar, 2020). Unlike from SO4, bicarbonate is present in groundwater at high quantities. It is created when carbon dioxide dissolves and produces a substantial amount of bicarbonate, which then dissociates to form weak carbonic acid and free protons (H). A crucial element in controlling the pH of groundwater is HCO3 (Herman & Gellasch, 2021).

The oxidation of nitrogen to nitrate is another chemical reaction that takes place in the atmosphere. Little levels of NO3 are naturally present in groundwater due to atmospheric nitrogen that is present in precipitation and minerals. However, human impacts can cause NO3 to find its way into groundwater. Urban yards, animal dung, excessive fertilizer use, and septic systems can all add to the amount of NO3 that enters groundwater (Mas-Pla & Menció, 2019).

According to researchers, determining the hydro-geochemical processes influencing the hydro-chemical facies of groundwater can be made easier by comprehending the fluctuation in main ions.

2.2. Distribution of F^- Concentration in Awash River Basin

Groundwater interacts with different minerals and rocks as it passes through geological formations. The dissolution and precipitation of minerals can result from these interactions, changing the groundwater's chemical makeup (A. Mohamed et al., 2022). Water chemistry influences both the stability of intermediate states and the creation of excited states, which in turn influences reaction rates (Hinman & Hinman, 2013). For instance, minerals like calcite, gypsum, or halite can dissolve in groundwater and enrich the water with specific ions. Rock-water interaction is strongly suggested by dissolved silica, fluoride, and alkalinity, whereas nitrate and depth to the water table reveal the effects of surface pollution sources (Lakshmanan et al., 2003).

According to Furi et al (2011), the East African Rift System is one of the most well-known volcanic belts in the world that is linked to high fluoride concentrations (Furi et al., 2011). High fluoride levels in lakes and the water supplies used by municipalities, estate farms, and other entities, and the potential health effects. The Middle Awash Basin's groundwater has fluoride concentrations ranging from 0.1 to 72.5 mg/l, which are determined by the amount of geothermal activity along the groundwater flow routes and the heterogeneous distributions of fluoride-bearing minerals. Fluoride is linked to thermal fluids and non-calcium waters of the $Na\text{-}HCO_3$ and $Na\text{-}Cl\text{-}SO_4$ types, particularly those with a high pH found in the rift floor near the basin's center, according to the results of the multivariate statistical analysis. According to the researcher result, F enrichment is caused by geological events involving a cation exchange reaction in groundwater as a result of the reaction process's removal of Ca^{2+} from solution. Approximately 60% of the water samples analyzed exceeded the WHO standard of 1.5 mg/l for fluoride, indicating a notable health risk for local communities. The study identified a heterogeneous spatial distribution of fluoride, with higher concentrations found in groundwater sourced from non-calcium bearing aquifers, particularly in areas associated with geothermal anomalies. Additionally, the enrichment of fluoride was linked to cation exchange processes that remove calcium (Ca^{2+}) from groundwater, resulting in increased fluoride levels as water flows from highland regions to the rift floor.

2.3. Ionic Exchange and Anthropogenic Influences on Groundwater Chemistry

According to numeral authors the exchange of ions is because of the physical and chemical factors. These processes have the power to change the chemistry of water(Ibrahim et al., 2019). Thus, flaws or ionic substitutions inside the crystal lattice, as well as chemical dissociation events that take place on a particle's surface generate the surface charge. Because colloidal particles have a significant electrical charge in relation to their surface area, they are typically the only particles with ion exchange sites(Catania, 2022).

Association half reactions, which incorporate ion exchange, enable the dynamic dynamics of the exchange process to be simulated. The process of exchanging ions in groundwater with ions on the surface of solid particles, like minerals or clays, is known as ion exchange. Depending on the makeup of the solid components, this process may cause some ions to be released or removed from the groundwater(Mondal et al., 2010).

The term "anthropogenic influences" describes how human activity affects the geochemistry of groundwater. These operations may introduce pollutants, modify organic hydro-chemical cycles, and have an impact on groundwater supply and quality. Various toxins can be introduced into groundwater by human activity(Long et al., 2012). Anthropogenic activity, such as commercial, industrial, agricultural, and domestic ones, can significantly alter the composition of water. These contributions may originate from activities that take place on the surface of the ground, including the use of household goods and industrial trash(Devic et al., 2014).

It has been observed that the use of chemical fertilizers in agriculture has increased the quantities of nitrate and sulphate in groundwater. Due to wastewater disposal, industrial and urbanization development have also shown to be a significant source of high quantities of trace metal introduction. Pollutant inputs can also originate below the surface of the ground, through contaminated recharge inside shallow aquifers, wells, and septic systems(M. M. Mohamed & Elmahdy, 2015).

The discharge of contaminants including heavy metals, organic chemicals (like pesticides and petroleum hydrocarbons), nutrients (like nitrates and phosphates), and synthetic compounds (like chlorinated solvents) can result from industrial processes, agricultural methods, and inappropriate waste disposal. The hydro-chemical makeup of groundwater can be dramatically changed by these pollutants. The geochemistry of groundwater can be affected by changes in land use, such as urbanization or deforestation (Sadeghi et al., 2021). Higher impermeable surfaces in urban areas usually result in decreased infiltration and higher surface runoff. As a result, runoff may contain higher than usual amounts of contaminants, such as metals, hydrocarbons, and fertilizers, which may eventually seep into groundwater. Chemicals used in agriculture, such as pesticides and fertilizers, can seep into the groundwater. Fertilizers often include nitrate, which is especially dangerous as it may contaminate groundwater (Craswell, 2021). Additionally, pesticides have the ability to linger in groundwater and alter the hydro-chemical processes that determine the groundwater resources' quality.

2.4.Chemical Characteristics of Groundwater

Geology and groundwater are typically related; the chemical properties of groundwater are determined by soil composition and geological structure. Additionally, the chemistry of groundwater is frequently influenced by outside factors like human activity, industrial effluents, and agricultural practices. Three types can be distinguished by hydro-chemical analysis of groundwater. They are meteoric, juvenile and connate. The most abundant portion of groundwater is meteoric water which is derived from precipitation i.e. rain and snows. It may include water from rivers, ice melt and lakes which are indirectly derived from precipitation. Connate waters are called fossil water, which were accumulated or entrapped in the sedimentary rocks at the time of deposition. They are two types distinguished epigenetic and syngeneic connate water. Connate water usually not developed for water supplies. This is because of its high salt concentration. Juvenile water usually known as magmatic water, when magma cooling. It contains water vapor and gases. Water vapor separate from magma and moves upwards the earth's surface from high temperature and then it condensed into superheated water.

2.5. The Role of Hydro-chemical Processes in Shaping Groundwater Composition

As a result of liquid water interacting with other solids, liquids, and gases at different stages of the hydrologic cycle, groundwater acquires its chemical properties(Appelo & Postma, 2005). Consequently, the chemical reactions brought on by both solutional and decompositional processes determine the composition of water. These procedures involve a variety of potentially highly complicated chemical systems. Numerous studies have demonstrated that the main factors influencing the composition of groundwater are hydro-geochemical processes. Since precipitation infiltrates through soil into the flow channels within the underlying geology, rain or snowmelt is almost always the primary source of groundwater recharge. Various chemical processes that take place as groundwater moves along flow pathways from original recharge sites to discharge areas affect its composition(Díaz-Puga et al., 2016). Thus, precipitation chemistry, water-chemical interactions as it flows through the flow route, interaction with lithological and stratigraphical frameworks, and other artificial controls result in the majority of chemical reactions.

It is generally accepted that the concentration of chemical constituents is related to the groundwater's residence durations and flow path extent. For instance, water that moves slowly or stagnantly is probably going to contain more ions than water that moves quickly over the same distance and through a comparable aquifer matrix(Tweed et al., 2006).

Chebotarev was the first to create the process of characterizing and categorizing different types of water based on major ion concentrations(Chebotarev, 1955).

The idea of "hydrochemical facies" was later developed as a result of the advancements made in this field.

Reviewing concepts related to rainwater chemistry, carbon dioxide in the soil zone, mineral dissolution and solubility, ion exchange, evaporation, oxidation, and reduction, as well as other unnatural controls like anthropogenic activities, is crucial given the natural processes that can affect the chemistry of groundwater in basalt aquifers(Catania, 2022).

It should be mentioned that when CO_2 charged water penetrates the soil zone and comes into contact with minerals that are soluble in H_2CO_3, mineral weathering may result(Chorley, 2019)[i].

Water-mineral reactions use up H_2CO_3. As a result, when precipitation seeps into the soil, it can trigger hydro-chemical reactions that produce acidity on a constant basis. These reactions then encourage weathering processes, which release ions into solution. Therefore, hydro-chemical processes in the soil are crucial in controlling mineral-water reactions by influencing the reactivity of fresh water from recharge events during infiltration(Egbueri et al., 2019; Ganyaglo et al., 2011). When minerals come into contact with water, they start to dissolve and keep doing so until the water reaches equilibrium concentrations or the minerals are entirely consumed. When they interact throughout the flow path, the minerals that the groundwater encounters may react at varying rates. This is due to the fact that minerals have a wide range of solubility. For instance, compared to the groundwater residence time, minerals like gypsum, halite, fluorite, and the majority of carbonate minerals are highly soluble and typically reach equilibrium quickly. Reaction kinetics must be taken into account since minerals like silicates react more slowly and will never reach equilibrium at low temperatures(Appelo & Postma, 2005; Catania, 2022; Varol & Davraz, 2014).

Significant concentrations of thermodynamically unstable silicate minerals, which weather or breakdown into clays and oxides when exposed to water, are present in basalt. Silicate minerals dissolve from their parent material due to chemical weathering, although the pace at which this happens is determined by the mineral's chemical structure(Baker & Neill, 2017; Hadnott et al., 2017).

2.6. Impact of Hydrochemistry on Groundwater Evolution and Water-Rock Interaction Dynamics

The chemical makeup of water, or hydrochemistry, is a key factor in the hydro-chemical evolution of groundwater. Over time, the chemical properties of groundwater can be influenced by the interaction between water and geological minerals. According to Sabarathinam and Ramachandran (2011), the minerals contained in the aquifer materials may dissolve and precipitate differently depending on the hydrochemistry of the groundwater.

Certain ions from the minerals may leach or dissolve into the groundwater when it comes into contact with rocks and minerals, changing the chemical composition of the water(Sabarathinam & Ramachandran, 2011). This process can eventually cause soluble minerals to dissolve and new minerals to precipitate, which will have an impact on the groundwater's hydro-chemical evolution. It may have an effect on the volume and pace of water-rock interaction. The amount to which the surrounding geological formations are weathered and altered chemically can be influenced by the composition of groundwater, including its pH, dissolved oxygen level, and presence of certain ions. Different elements may be released or taken up as a result of water-rock interactions, changing the hydro-chemical composition of groundwater(Al Haj et al., 2023).

2.7. Multivariate Statistical Methods and Conventional Techniques

Several authors used multivariate statistical method to interpret tasted samples. There are numerous statistical and graphical methods for deciphering data on groundwater quality. In groundwater research, chemometric approaches are applied to draw conclusions based on statistically significant variables in the variability of water quality data (Loganathan et al., 2015). As a result, when examining changes in hydro-geochemical data, analytical findings and geographic information will not only be useful in interpreting patterns, but also in establishing new understanding when chemometric techniques are applied (Papaioannou et al., 2016).

Usually, one must ascertain the distribution of the data set prior to utilizing any chemometric technique. This is due to the fact that many approaches presume that the data's underlying population is regularly distributed Skewness and kurtosis are typically measured in order to determine whether a normal distribution exists. The distribution's asymmetry with respect to the mean is measured by skewness, while the density's peakness is determined by kurtosis (Boylan & Cho, 2012).

The term "conventional techniques" describes the standard approaches to groundwater resource management (Gee & Hillel, 1988; Nigam & SM, 2019; Rogers & Chung, 2017). Among these techniques is well logging, which uses boreholes to measure and document the chemical and physical characteristics of subsurface formations.

Another important method is pumping tests, which measure the drop in water levels in observation wells as water is pumped from a well in order to evaluate the characteristics of the aquifer. Hydraulic conductivity testing, which frequently employs techniques like slug tests or continuous head tests, ascertains the ease with which water can pass through rock or soil. Sampling water quality is a crucial step in gathering and examining water samples to evaluate the chemical, biological, and physical properties of groundwater. Aquifer mapping also makes use of spatial data and geological studies to produce maps that show the features, depth, and extent of aquifers.

Aquifer mapping also makes use of spatial data and geological studies to produce maps that show the features, depth, and extent of aquifers. Groundwater modeling, which frequently makes use of traditional software tools, uses mathematical models to simulate groundwater flow and transport processes. These methods collectively serve as the cornerstone of hydrogeology, assisting experts in the comprehension of groundwater systems, the administration of water resources, and the resolution of contamination problems.

The study gap for the hydro-chemical evolution of groundwater can vary depending on the specific context and research objectives. A major research gap in hydro-chemical groundwater assessment is the scarcity of current, thorough data. This might be due to a lack of information on the physicochemical characteristics, major and trace element concentrations, and contaminant levels of groundwater. To close this gap and offer a more precise and up-to-date evaluation of groundwater chemistry, a large dataset must be gathered and thoroughly examined. A number of variables, including geological heterogeneity, hydrological conditions, and human activity, can cause considerable regional and temporal variability in groundwater chemistry. Studies that sufficiently capture this heterogeneity, particularly at the local or regional size, could be lacking, nevertheless. To close this gap and record the temporal and geographical variability in groundwater chemistry, an extensive and methodical sampling program covering several sites and seasons must be carried out. Based on the specific context of the Modjo River Basin in Central Ethiopia, the study gap for the hydro-chemical evaluation of groundwater in this region may include limited hydro-chemical data, understanding natural and anthropogenic controls, spatial variability and pollution source.

Although conventional techniques are frequently used in groundwater research, multivariate methods may not be applied in the hydro-chemical assessment of groundwater in the Modjo River Basin. Principal component analysis (PCA), cluster analysis, factor analysis, and other multivariate approaches can be used to find patterns and correlations between various hydro-chemical variables. Multivariate approaches can offer a more thorough knowledge of the hydro-hydro-chemical processes and factors influencing groundwater chemistry by concurrently integrating and evaluating several variables. Studies that have used these sophisticated statistical methods in the unique setting of the Modjo River Basin, however, may be few in number.

CHAPTER THREE

METHODS AND MATERIALS

This study is based on water sample analysis together with the utilization of existing geological and hydrogeological information. This research's main goal is to evaluate gathered chemical data that used to understand the main factors influencing groundwater composition as it interacts with various lithological and stratigraphical frameworks. A number of approaches have been taken into consideration in order to accomplish the thesis work. The approach followed includes desk study, field work, laboratory analysis and data interpretation.

3.1 Desk study

Prior to the actual field work, compilation of a report on the relevant published resources pertaining to the tasks under investigation was undertaken. This includes publications on the meteorology, groundwater (hydrogeology), water quality data, topography, surface and subsurface geology. The collected data include publications, maps, reports, satellite images, well data etc.

3.2 Sample collection and in-situ parameter measurement

Following the examination of the collected previous data (location, depth to water table, productive horizons, etc.) on the available wells in the Modjo river catchment, the selection of the water points was undertaken to conduct water sampling. Before the field trip, the required analyses (e.g. Anions and cations,) and sampling equipment (e.g., size and types of sampling bottles etc.) was identified. Accordingly, 79 groundwater samples were collected for chemical analysis. All 79 were borehole. They classified into three regions based on their elevations (upper Modjo, Middle Modjo and lower Modjo. Their codes were derived from their names (UM-upper Modjo, MM-miidle Modjo and LM-lower modjo). Additional measurement in the field was also conducted (e.g., pH, and conductivity).

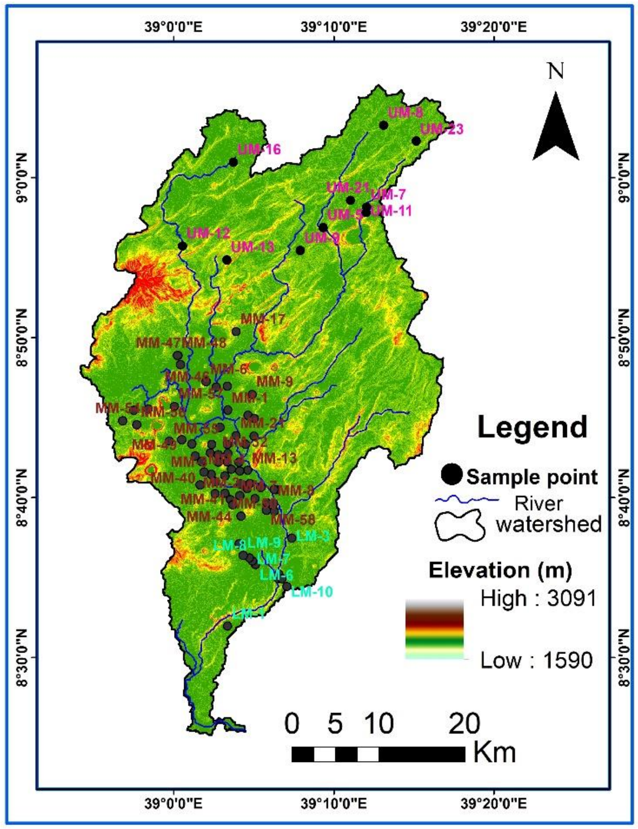


Figure 3: 1 Sample location

3.2.1 Accuracy of Chemical Analysis

The accuracy of major anions analysis can be estimated from electrical balance. This concept is used to check the correctness of analysis,

This cation- anion balance is calculated in order to determine the electric neutrality of solution

$$\text{Electrical Balance (E.B., \%)} = \frac{(\Sigma \text{ cation} + \Sigma \text{ anion})}{(\Sigma \text{ cation} - \Sigma \text{ anion})} * 100$$

$$= \frac{595.577 + (-585.851)}{595.577 - (-585.851)} * 100 \quad \mathbf{= 0.82\%}$$

The error value of Electrical Balance of up to 2% is acceptable in almost all laboratories. Sometimes the error more than this number is not accepted, but with deviation in excess of 5% the sampling and analytical procedures should be examined (Appelo & Postma, 2004).

For this analysis, cations and anions were expressed as meq/L and listed with their charge sign. The sums of cations were from Na^+, K^+, Mg^{+2}, Ca^{+2}, while the sums of anions were from Cl^-, HCO_3^-,NO_3^-, F-, SO_4^{2-}(Appendix 3).

3.3. Methodology

3.3.1. Laboratory Analysis

These tests aim to identify various chemical, physical, and chemical characteristics of the groundwater. It entails evaluating gathered materials with various procedures in order to determine certain hydro-chemical properties. The chemical determining of the parameters conducted in Engineering Corporation of Oromia (ECO). The hydro-chemical laboratory analysis involves the submission of collected samples to a qualified laboratory, adhering to the study objectives. For this study there were assessments of major and minor ions.

Total dissolved solid (TDS) determined by total dissolved solids dried at 180^{o}c. The concentration of sodium and potassium in water sample were determined by flame emission photometer, whereas calcium was determined by EDTA Titrimetric Method, magnesium measurements identified by using the Atomic Absorption Spectrophotometer (AAS) Method. Determination of chloride is easily made by Argentometric method. Both carbonate and bicarbonate were determined by Titration method. Sulphate , nitrate, and fluoride were determined by Turbidimetric method, HACH Cadminium Reduction method, and Ion-selective electrode method respectively.

3.3.2. Data Analysis and Interpretation

Data analysis is a critical step in the determination of major geological processes. It involves processing and interpreting the collected data to identify patterns, relationships, and the dominant hydro-chemical processes occurring in a given system. The laboratory analysis of the obtained water samples looked at a number of factors. Using the proper statistical tools, data from the laboratory analysis were statistically examined.

The method employed for this thesis involved interpreting data using Python-based workflows, specifically leveraging Google Colab popular platform among students and educators due to its convenience and efficiency (Baptista, 2021; Bisong & Bisong, 2019; Naik et al., 2022).

Google Colab offers a pre-configured Python environment that simplifies the development process by eliminating the need for local setup. This environment comes with essential libraries and packages, allowing users to focus directly on project goals without spending time on technical configurations.

One of its most useful features is the ability to upload data files directly into the notebook. Additionally, seamless integration with Google Drive ensures smooth and organized access to project files, eliminating the need for manual file management and improving workflow efficiency. By simplifying technical processes and providing an intuitive interface, Colab significantly enhanced the productivity and effectiveness of my research. This combination of features not only streamlined the technical aspects of my thesis but also enabled a more organized and efficient workflow, ensuring the successful completion of my research objectives.

3.3.2.1. Multivariate statistical analysis

The primary hydrochemical species, hydrochemical processes, and water flowpaths crucial to ground water evolution are all revealed by the application of multivariate statistical methods (MSMs) to ground water chemistry. All statistical analysis operations were carried out using Past and IBM SPSS software. For this work; ten variables (Na, K, Mg, Ca, Cl, SO_4, HCO_3, NO_3, pH, TDS, and EC) were examined. These factors were selected because they are the most common components used to describe groundwater. The variable's mean was utilized in cases where values were absent. First, descriptive statistics were calculated, encompassing mean, standard deviation, minimum, and maximum values. To find out how the variables correlate, Pearson's Correlation Matrixes were created.

Principal component analysis

Principal component analysis, or PCA, was employed to reduce the amount of data. Standardization of the data was done to avoid the impact of different scales. Next, components having eigenvalues higher than one were selected.

The varimax rotation was used to the primary components to identify factors that can be more easily described in terms of hydro-geochemical processes, as it maximizes the variation of each component. The correlation matrix's primary components were taken out. The variables and samples were then grouped into similar categories using hierarchical cluster analysis (HCA) on the data. By using this analysis including box plot different plot had done to explain the hydro-chemical evolution of groundwater of the study area.

3.3.2.1. Hydro-chemical Plotting

This is for constructing hydro-chemical plots such as Piper diagrams, Stiff diagrams, or ternary diagrams to visualize the major ion composition and identify water types or hydro-chemical trends. There are different plots that deal with water types, major ions. For this purpose the plots are developed using Past software and Python.

3.3.2.3. Cluster Analysis

Cluster analysis can play a significant role in understanding the hydro-chemical processes of groundwater by identifying patterns and grouping similar samples together. Cluster analysis can be used to handle large water quality datasets, and identify the dominant mechanisms and factors controlling the geochemistry of groundwater. Various samples are compared using various factors, and the samples are then categorized based on how "similar" they are to one another. This method is frequently used in water-chemistry studies to identify sample groups with comparable chemical and physical properties. Google clob system was used for GW cluster analysis in this study. Figure 3.2 illustrates the comprehensive flowchart detailing the processes involved in hydro-chemical data collection, analysis, and interpretation.

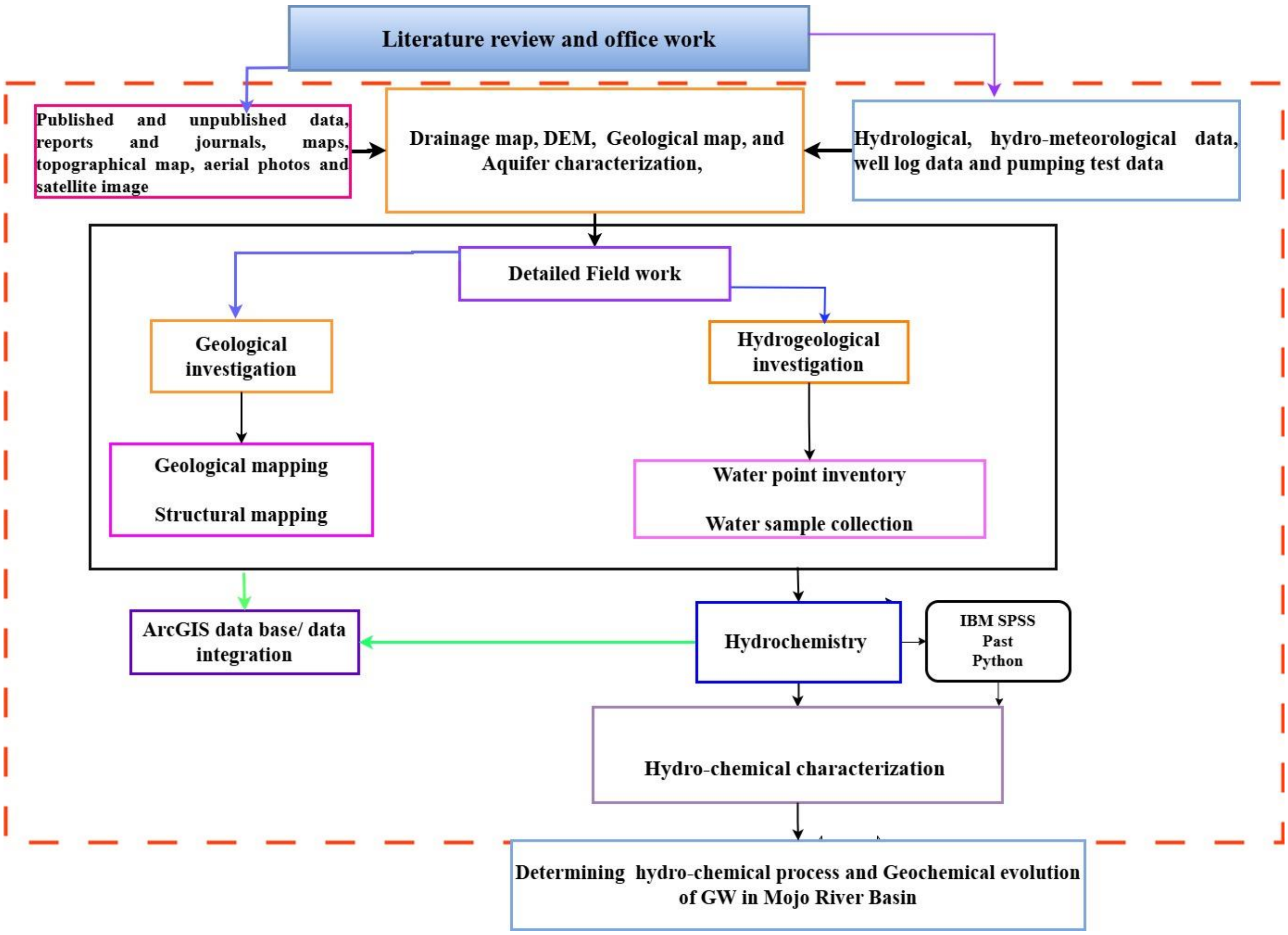


Figure 3: 2 Methodology flow chart

3.4. Materials use

Specific materials may vary depending on the project's scope, budget, and analytical requirements. It is important to select the appropriate materials and methods to ensure the quality and reliability of the hydro-chemical data. For this research, there was using of PH meter (to measure hydrogen power of water sample), EC meter (to measure water's ability to conduct electricity). To achieve the goal of this study ArcGIS 10.8, Python, Past Software and IBM SPSS were the main software used for this research work.

Table 3: 1 Software and their purposes

No.	Name of software	Purposes
1.	ArcGIS 10.8	Data processing and map preparation software. For spatial analysis and visualization
2.	IBM SPSS statistics	For statistical data analysis, tabulations and graphical representations
3.	Python	Analyzing and interpreting hydro-chemical data related to groundwater, plotting different diagrams
4.	Past	For geochemical modeling and cluster analysis

CHAPTER FOUR

GEOLOGY AND HYDROGEOLOGY OF THE STUDY AREA

4.1 Regional Geology

Ethiopia's current morphology, physiography, and geological settings are the consequence of two significant post-Paleozoic events, which were succeeded by significant volcanic activity periods (Mohr, 1971). The extrusion of the Trap Series succession (plateau volcanism) resulting from the related fissure volcanic activity is regarded as the up-doming (Mohr, 1971). The Afro-Arabian Dome was created by the first tectonic event that took place in the late Mesozoic early and Tertiary period. Fissure volcanic activity that resulted from this event led to the extrusion of the Trap Series succession (plateau volcanism), which is thought to be the up-doming (Fikirie et al., 2020; P. Mohr & Gouin, 1976).

The second tectonic event resulted in rift development and related volcanic phenomena during the late Tertiary-Quaternary period. The Ethiopian Rift is genetically related to the Great Rift Valley of East Africa. The major and largest volcanic episode on both the South Eastern and the Western plateau of the pre-Miocene period was the extrusion of the Trap Series fissure basalt during the Eocene-Oligocene time (Kazmin & Seifemichael, 1978).

Nazareth group consists of a thick succession of ignimbrite, unwedded tuffs, ash flows, rhyolites, and trachytes that outcrop mostly on the rift floor reaching a thickness of more than 250 m. According to Kazmin and Seifmicheal(1978), this group name was used informally for lower welded tuff (related to Werchecha trachyte volcanism), Aphanitic Basalt (which exhibits vertically curved columnar jointing along with sub-horizontal sheet jointing), and upper welded tuff (related to Yerer volcanism) (Basabe & Bedir, 2007; Kazmin & Seifemichael, 1978).

The Awash Gorge near Kereyu Logde contains young olivine porphyritic basalt that dates to 2.8 million years ago. It is distinguished by large vesicles filled with calcite. Unlike younger units, the Bofa Basalts are evenly distributed over the rift floor and represent an episode of fissure eruption that immediately followed a major faulting (Morbidelli & Piccirillo, 1973). The Bofa

Basalts may include even older flows, for example an age of 3.5myr, which was established by Mohr (1971) for Basalts in the Nazareth region which possibly belong to the same unit.

Wonji group **is** cluster of volcanic activity that associated with the axial extensional zone of the Wonji fault belt. While there are occasional volcanic events, such as basalt eruptions and central volcanoes, that take place outside of this belt, the majority of volcanic activity during the Pleistocene-Recent period is undeniably influenced by this tectonic characteristic as noted by numerous authors (Mohr, 1971).

Kazmin and Seifemichael (1978) have identified the name "Wonji group" as referring to various geological formations, including Dino ignimbrites, Pentelleritic volcanic centers, and recent basaltic fissures. Additionally, the group includes minor units such as hyeloclastites, explosion centers, and rhyolite domes.

Ancestral Lake is thought to have blanketed Mojo and the surrounding area during the Quaternary pluvial period. This sizable ancestral lake's deposition produced the lacustrine sedimentations(Mohr, 1971). The Wonji volcanic and the lacustrine rift deposits are of the same age. They mostly consist of tuffs and volcanic clastic deposits containing silts, clays, and diatomites, with silts and clays predominating. In the Rift, alluvial deposits are also typical; they are connected to flood plains and, in certain areas, combined with clastics from volcanoes (Basabe & Bedir, 2007).

4.1.1. Tectonics

A region of continental break-up that accommodates the relative movement between the African and Somalian Plates, the East African Rift System (EARS) was created when the brittle African continental "plate" responded to stretching forces caused by very slow creep of rocks hundreds of kilometers deep in the Earth. Since it links the Kenya Rift and the Afar depression, the Main Ethiopian Rift (MER) is a crucial region within the Ethiopian Archipelago (EARS).

The NE-SW border fault system and the N-S to N20°E-trending system, which are made up of en-echelon right-stepping faults that indirectly affect the rift floor (Wonji Fault Belt, WFB) are the two fault patterns that make up the MER. Up until historical times, there has been strong volcanic activity consistent with the MER tectonic development, with a characteristic bimodal composition. The primary early events of the MER opening, which occurred approximately 6.5 Ma, may have been connected to these explosive deposits, according to correlations between pyroclastic deposits found inside the rift depression and on the rift shoulders. The NE-SW trending boundary faults and associated fractures developed during this initial phase of rifting, which was linked to a NW-SE extension direction. Important off-axis volcanoes occurred on the MER shoulders during this rift episode as a result of a lateral, extension-parallel flow of magma from below the rift depression. An additional (Quaternary) stage of oblique rifting with a left-lateral component of motion along the rift axis was identified by a shift in the extension direction from E-W to ESE-WNW. The WFB system developed as a result of this oblique rifting. Analog modeling further supports the explanation that the dextral components of displacement along some WFB faults are attributable to a counter-clockwise block-rotation internal to the deformation zone. In addition, the Quaternary stress field reorientation greatly decreased the off-axis volcanic activity by preventing magma from being transferred laterally. The formation of the newly-formed enechelon oblique and strike-slip faults of the WFB, in particular, during the second oblique phase, limited the rise of melts along the rift axis and encouraged the concentration of volcanic activity along the en-echelon WFB segments.

4.2. Local Geology

Many workers in numerous areas of the rift valley have conducted a number of local and regional geological studies. However, the Ethiopian Rift geological map provides the majority of the local geological data required for such purpose(Kazmin & Seifemichael, 1978). The study region is mostly covered by two types of rock characterizing the geology in exclusive terms (volcanic rocks and volcano-sedimentary deposits).

4.2.1. Recent to sub recent Rhyolite domes and flows

It's a compact, porphyritic rhyolitic lava flow that makes up a minor portion of the study area. It is located in the central part intercalated inside the Bofa basalt and is thought to be the residual wall of the Pleistocene-era volcanic tectonic sub-circular collapse (Dechasa, 1999).

4.2.2. Basalts

The southeast portion of the research area is where Basalt found. The unit forms the upper portion of NE trending escarpments and covers the Nazret unit inside the intra-Rift complex. Rare plagioclase-rich basaltic andesites are also discovered, but olivine basaltic composition predominates in lavas. The texture of the basalts is porphyritic or subaphyric, and olivine typically makes up the phenocrysts. The age distribution is 2.7–1.8 Ma. Because of its stratigraphic location and makeup, the Tulu Rie Basalt is regarded as a component of the Bofa Basalt, which was studied by Kazmin and Seifemichael Berhe in 1978. Sub-horizontal or somewhat slanted tabular lava flows make up the TRB. At the Tulu Rie Basaltic Ridge in the southeast catchment, the largest thickness that has been observed is 20 meters.

The central, western, and northern regions of the research area are where Bofa Basalt found. It includes roughly 880 km2 of the research area. The unit is mostly composed of olivine, clinopyroxene, apatite, and uncommon basaltic andesites that are rich in plagioclase (Gezahagn Yirgu, 1980). The basalts have a vesicular, less worn and friable porphyritic or subaphyric texture.

4.2.3. Ignimbrites

It is grayish red in color, moderately to highly weathered rock units are medium to course grained with a kind of sheet flow structures and show eutaxitic texture with oblate glassy fragments sometimes with recrystallized rims. This is one of the youngest rock units found in the study area explained by the flow took place into preexisting valleys of the escarpment and it also climbs to mountains revealing that they occurred after trap series. This unit is a basal unit grouped under the intra Rift complex and may constitute the upper part of Nazret Group of Kazmin and Seifemichael Berhe (1978) with respect to age constraints.

4.2.4. Ash flows and welded tuffs

In the studied area, exposed ash flows create a thin layer of continuous horizontal stacking that is between two and thirty centimeters thick. and have a greenish gray hue. With additional fills, the fine-grained, compacted, welded tuffs have significant weathering at the top and less weathering at the bottom.

4.2.5. Lacustrine deposits and alluvial cover

Pliocene-Pleistocene ignimbrite is interbedded with lacustrine strata in the lakes region, on the rift shoulders generally, and in Mojo and its environs specifically (Mohr, 1966). The majority of them consist of redeposited volcanic sands, diatomite, siltstone, sandstone, calcareous elements, and intercalation of water-laid tuffs. Lake Koka, Lake Hora, and Lake Kilole are the closest lakes to where the deposition is located. They are located on a somewhat NE elongated dip in the area's central sector and make up around 30% of the exposed rocks. These deposits are often fine-to medium-grained, sparsely stratified, highly friable, and less compacted. Their hue is typically brownish-yellow.

4.2.6. Chafe Donsa pyroclastic deposits

Mostly consists of white pumice tuff, blue white pumice, white tuff, and pumice flow. The unit has a paleosoil unconformity and is composed of at least three strata at the type locality. There is regular grading in the unit as evidenced by the large amount of lapilli in the bottom half and pumice in the upper part. East of Sire town, the unit unconformably overlies Dino ignimbrite and is composed of pumice tuff, tuff, and paleosoil. It is dispersed over Mojo, Dire, Sire, and northeast of Adama towns, with a type locality of more than 70 meters. The Boru River, roughly 10 kilometers east of Dera Town, is its type location.

4.2.7. Tarmaber basalts

Consist of tuff breccia and large aphyric basalt lavas. The unit unconformably covers Debre Birhan ignimbrite at the type locality. The unit at Balchi is unconformably layered on top of Debre Birhan ignimbrite and unconformably layered on top of Nazret pyroclastic deposits. It’s distributed in the Kesem river basin with more than 20 m at the type locality.

4.2.8. Nazreth unit

This unit is divided into two lithological facies: the upper part is composed of white to bluish-gray rhyolitic compacted tuff and tuff breccia that contain white pumice, rhyolitic lava fragments, crushed and/or slightly weathered obsidian fragments, and rare reddish-brown basaltic lava fragments. The lower part is composed of yellowish-white pumice fall deposits, tuff, crystal tuff, and an alternation of fine volcanic sands and pumiceous tuff.

4.2.9. Tullu Re'e basalts

The unit consists of black aphyric basalt lavas. At the type locality, it unconformably overlies the Nazret pyroclastic deposits. This basalt unit has a northeast-southwest distribution, extending from the hills north of Mojo town to Ejere town. In the type locality at Kunche (L-MAD06), the unit has a thickness of more than 15 meters. The unit is classified as the Bofa basalts in GSE (1978) and as the Tulu Rie Basalts unit in F. Mazzarini et al. (1999).

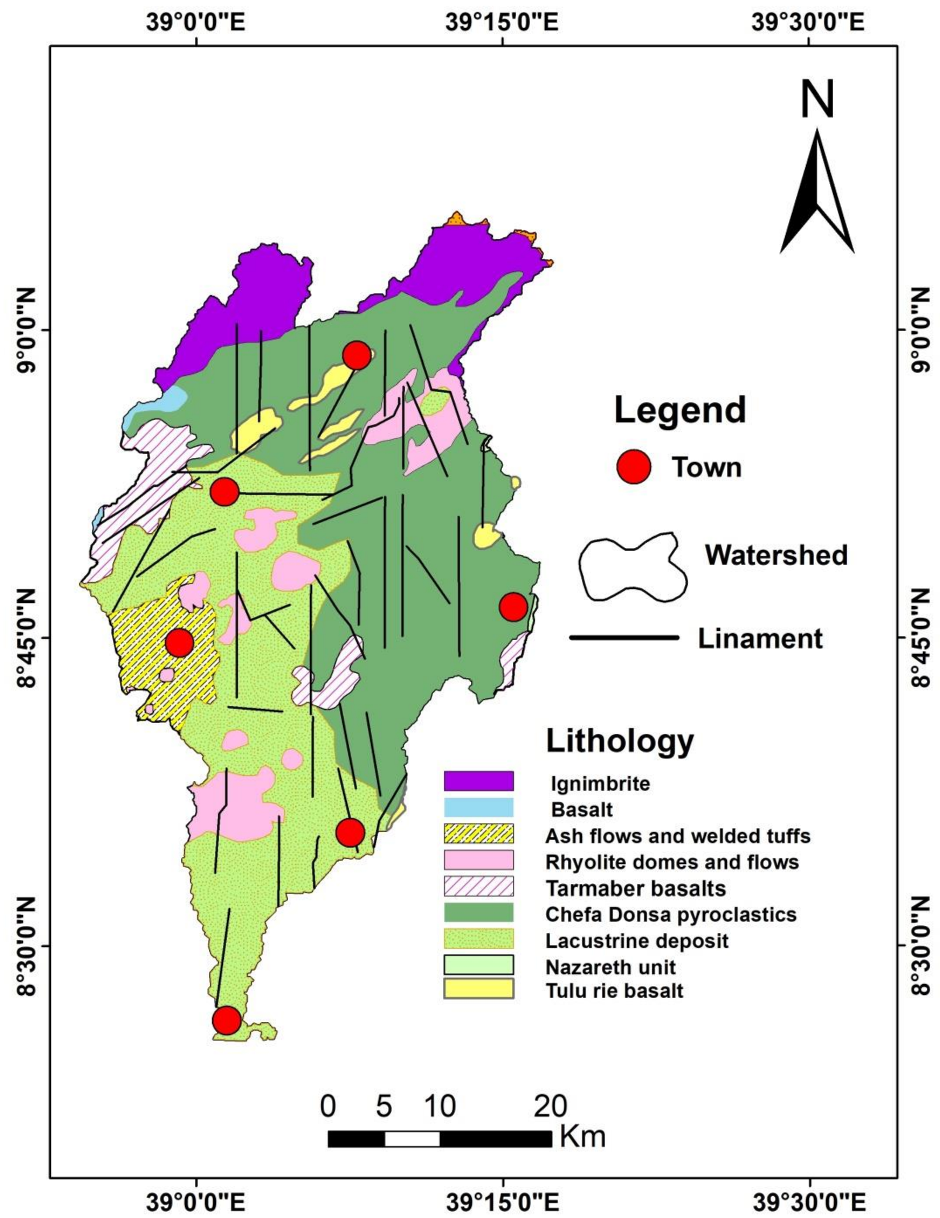


Figure 4: 1 Geological map of study area

4.3. Hydrogeology of Study Area

The Modjo River Basin, located in central Ethiopia, is a vital hydrological system supporting agriculture, domestic water supply, and industrial activities. It is primarily composed of volcanic rocks, such as ignimbrites, tuffs, and basalts, which are common in the Ethiopian Rift system. Depending on the extent of weathering and fracturing, these volcanic units create aquifers with different permeability. In certain places, groundwater storage is facilitated by alluvial deposits along the river valley (Ayenew, 2008).

Its hydrogeology is shaped by the region's geological setting, climate, and topography. Groundwater in the basin occurs in both shallow and deep aquifers, primarily within fractured volcanic rocks and alluvial deposits. Rainfall is the primary source of recharge, with infiltration being boosted in regions with permeable soil and shattered rocks. Streams and rivers that flow seasonally also aid in recharge. Springs, river base flow, irrigation and household wells are examples of discharge zones (Gebere et al., 2021; Sisay et al., 2023). There is a clear relationship between surface water and groundwater in the Modjo River. The river replenishes nearby aquifers during the rainy season, while groundwater supplies base flow to keep the river going throughout the dry season (Kawo & Karuppannan, 2018a). Groundwater movement in the basin is controlled by the permeability of the aquifers and the topographic gradient. Generally, groundwater flows from the highlands in the eastern and southeastern parts of the basin toward the lowlands, discharging into the Modjo River and eventually the Awash River system (fig 4.2). Local variations in flow direction can occur due to geological structures like faults and fractures, as well as human activities such as groundwater pumping. A conceptual hydrogeological model of the basin highlights the interconnected nature of its aquifer systems, with recharge occurring primarily through rainfall infiltration in the highlands and along riverbanks during the wet season (June to September). Groundwater discharges into the Modjo River, springs, and wetlands, with some flow potentially exiting the basin into adjacent hydrological systems. Both human activity and natural geological processes have an impact on the catchment's water quality. Groundwater mineralization is frequently moderately high in basaltic terrains, and urbanization and agricultural runoff can contaminate it, especially with phosphates and nitrates (Dalecha, 2021; Tekile, 2023).

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1. General

Hydrochemistry involves the analysis and interpretation of various chemical parameters and compounds present in water. Geochemical composition of groundwater is largely governed by natural factors (such as groundwater regime, mineralogical composition of rocks, climatic condition, relative groundwater flow velocity, the residence time) and anthropogenic activities (such as overexploitation of groundwater resources, agriculture, industry, urban development) (Appelo & Postma, 2004). The combined effects of these factors create diverse water types that vary spatially and temporally. The spatial variability observed in the composition of groundwater can provide insight into heterogeneity of aquifer as well as physical and chemical process controlling groundwater chemistry. Therefore, hydrochemistry helps to get an insight into the contribution of water-rock interactions and anthropogenic influences on groundwater composition and understanding of geochemical process that is crucial in terms of sustainable groundwater resource in Modjo river catchment. Detail description of hydro-chemical characteristics and geochemical processes that control chemical composition of water in the study area is presented in this chapter.

5.2 Physical parameters

The measured field parameters (pH, EC, TDS) together with analytical data for major ions are listed and presented in Table 5.1. The measured EC of all sampled water varies from 317 to 1554 µS/cm (figure 5.1 left). It is found that water samples taken from upper Modjo catchment have low mean EC value (488 which is <500µS/cm), whereas water samples taken from lower Modjo catchment have a mean EC value of 726 which is >500 µS/cm.

The standard EC value is in the range of 0-1000 µS/cm (). Hence, the EC value of the analyzed water sample fall in the range of standard set by WHO except for sample MM-16, MM-17 and

MM-18 which is greater than 1000 µS/cm. Values exceeding 1000 mg/L for EC suggest a high level of dissolved ions in the water, which can result from various natural and anthropogenic causes. Water that flows through mineral-rich rocks and soil may dissolve minerals such as calcium, magnesium, sodium, potassium, and sulfates, leading to higher EC levels. The pH value ranges from slightly acidic to nearly alkaline (6.41 and 8.52).

The measured TDS values in all water samples ranges from 194-1060 mg/l (Figure 5.1 right). The palatability of water with a total dissolved solids (TDS) level of less than about 600 mg/l is generally considered to be good; drinking-water becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 mg/l (WHO, 2018). Accordingly, the majority of water from the catchment falls within the range recommended by WHO guideline for drinking water quality except for MM-16 and MM-17 that exceeds 1000 mg/L (Appendix 3). The reason for this value is likely caused by a combination of natural and human-induced factors. Groundwater in areas with volcanic formations often has elevated TDS. The spatial distribution of EC is shown on Figure 5.1

Table 5: 1 Statistical summary of hydro-chemical components in the study area

Parameters	**Unit**	**Minimum**	**Maximum**	**Mean**
EC	(µS/cm)	317	1554	693.61
Ph		6.63	8.52	7.31
TDS	mg/L	194	1060	430.51
Na^+	mg/L	11.39	276	67.39
K^+	mg/L	3.1	36	13.05
Mg^{+2}	mg/L	2.3	36	17.87
Ca^{+2}	mg/L	6.71	174.8	56.90
Cl^-	mg/L	2	35.5	15.80
SO^{-2}_4	mg/L	0.1	114.14	18.68
NO^-_3	mg/L	0.03	85.5	7.65
HCO^-_3	mg/L	6.71	1000.4	405.00
F^-	mg/L	0.07	1.9	0.74

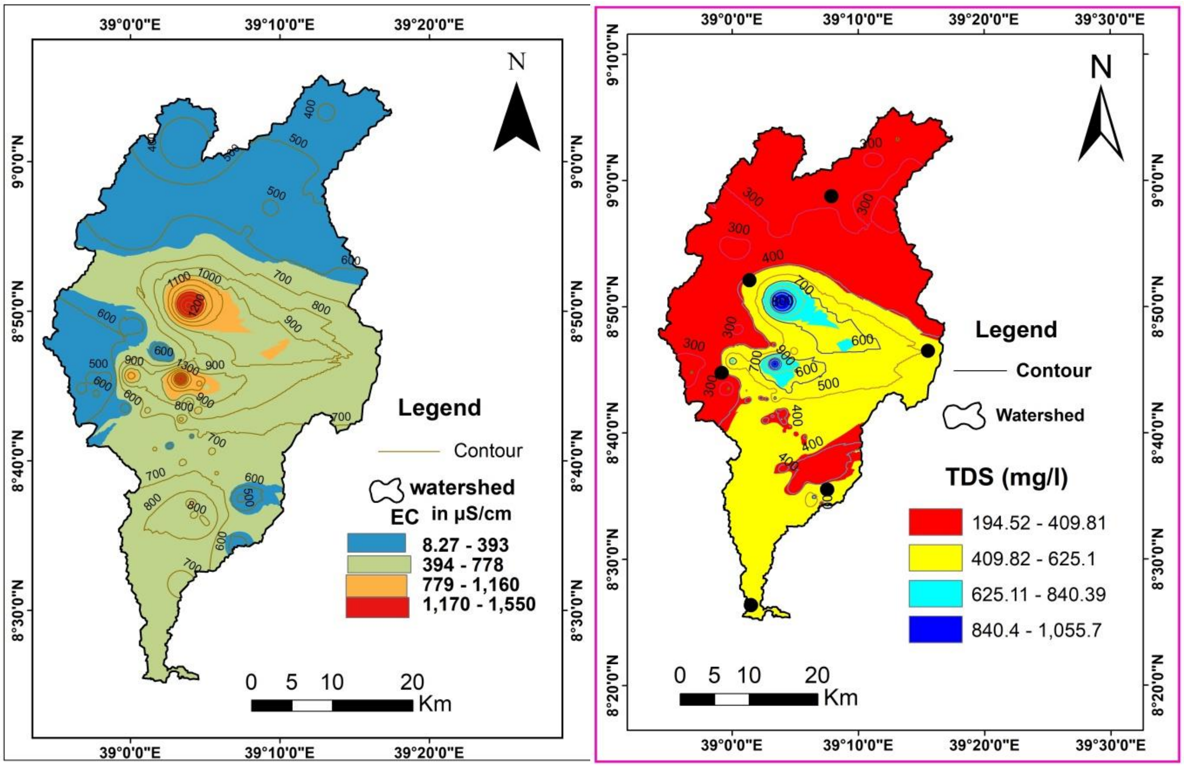
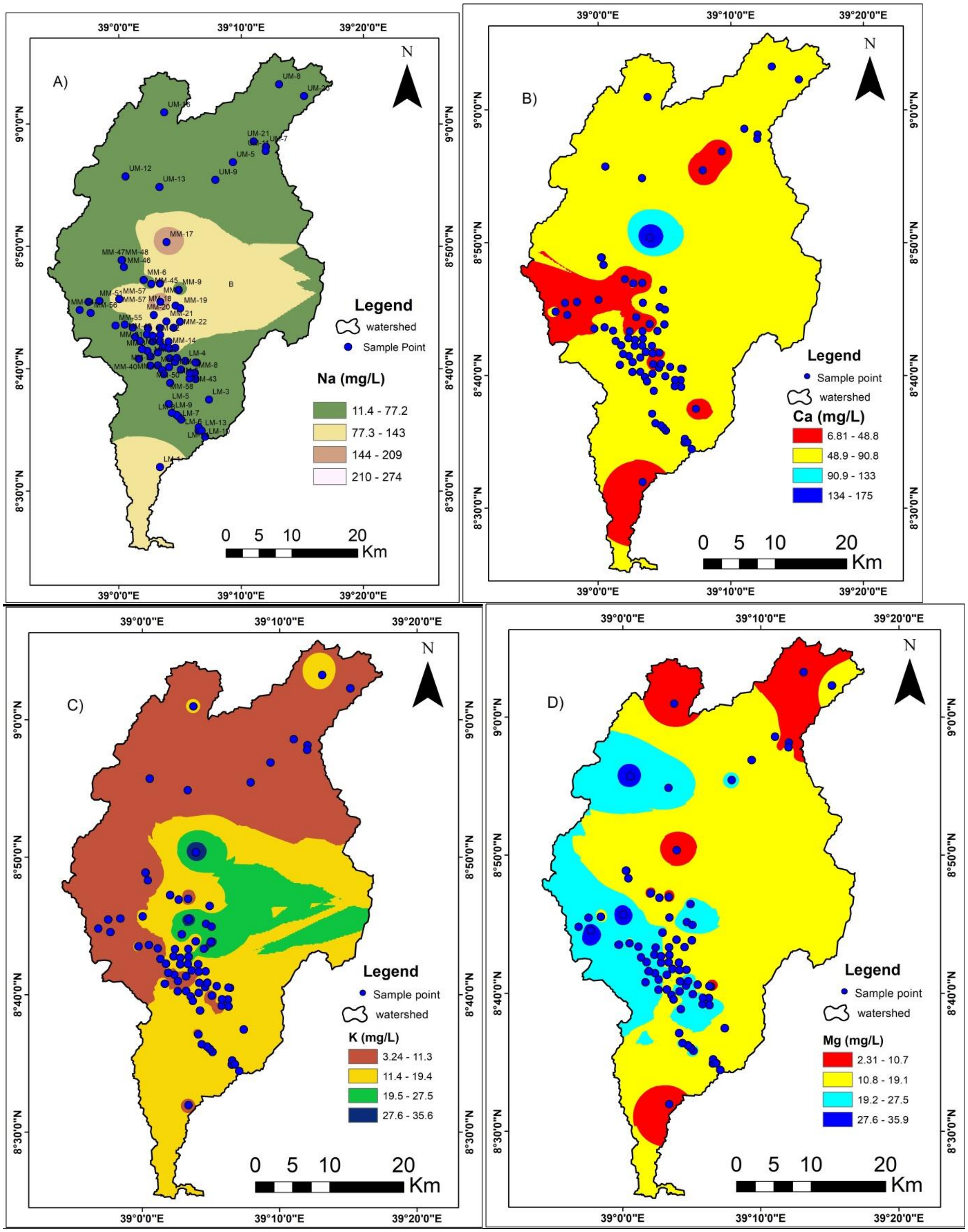


Figure 5: 1 spatial distribution of Electric conductivity and TDS

5.3 Major ions

Major ions found in groundwater provide information about its origin and quality. Mineral weathering and dissolution are the source of cations such as potassium (K^{+}), sodium (Na^{+}), calcium (Ca^{2+}), and magnesium (Mg^{2+}). Water hardness is influenced by calcium and magnesium, which are prevalent in shallow aquifers, whereas sodium predominates in deep aquifers. Carbonate rocks, seawater, fertilizers, or natural minerals are the sources of anions like bicarbonate (HCO_3^{-}), chloride (Cl^{-}), sulfate (SO_4^{2-}), nitrate (NO_3^{-}), and fluoride (F^{-}). Nitrate indicates pollution, whereas sulfate and chloride indicate salinity. Ionic strength, salinity, and alkalinity are measured by parameters like TDS, EC, and pH, which aid in determining if water is suitable for usage. The relative distributions of dissolved major cations and anions are explained and their variability in the area are shown in Figure 5.2.


A)
N
Legend
watershed
Sample Point
Na (mg/L)
11.4 - 77.2
77.3 - 143
144 - 209
210 - 274
0 5 10 20
Km
39°0'0"E
39°10'0"E
39°20'0"E
9°0'0"N
8°50'0"N
8°40'0"N
8°30'0"N
B)
Legend
Sample point
watershed
Ca (mg/L)
6.81 - 48.8
48.9 - 90.8
90.9 - 133
134 - 175
C)
Legend
Sample point
watershed
K (mg/L)
3.24 - 11.3
11.4 - 19.4
19.5 - 27.5
27.6 - 35.6
D)
Legend
Sample point
watershed
Mg (mg/L)
2.31 - 10.7
10.8 - 19.1
19.2 - 27.5
27.6 - 35.9

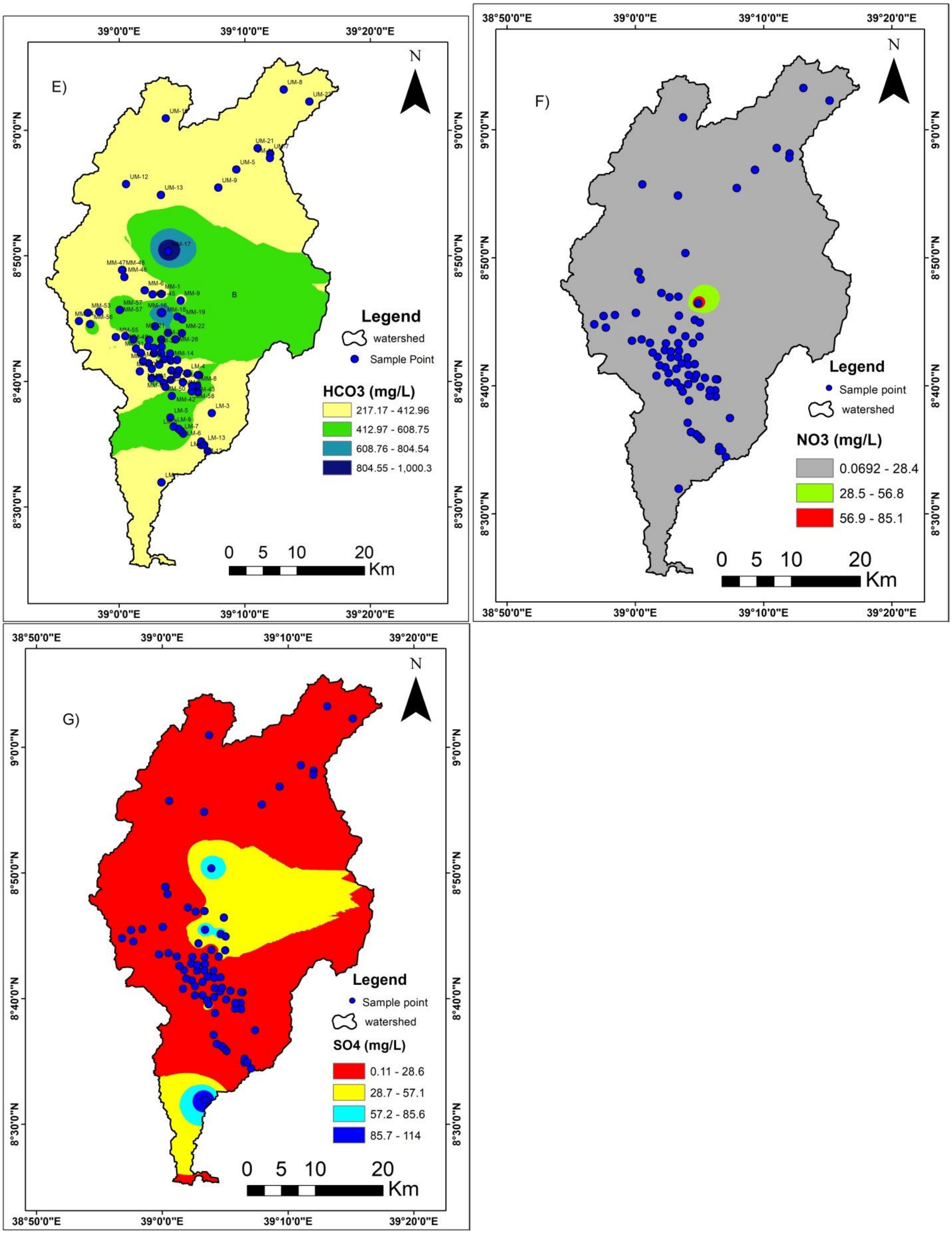


Figure 5: 2 spatial distributions of cations and anions

It is found that groundwater of the study area has Na^+ ions as the dominant cations, followed by calcium (fig 5.2 A&B). High relative Na+ content of groundwater is mostly referred to the deep aquifer, whereas high Ca^{2+} is prevailed in groundwater from the shallow aquifer. Volcanic regions can have significant hydrothermal activity, which alters minerals and can lead to the release of calcium into groundwater. The weathering of volcanic materials can release calcium into the groundwater (Morán-Ramírez et al., 2016). Dissolved anions of the groundwater are strongly dominated by HCO_3^-, followed by SO_4^{2-}(fig 5.2 E&G).

Accordingly, the chemical composition of analyzed groundwater is dominated by HCO_3^- and Ca^{2+} + Mg^{2+}or Na^+. High bicarbonate levels in groundwater are often due to a combination of volcanic gas emissions (CO2), mineral weathering, and hydrothermal processes (Lowenstern, 2001). Sulfate concentration ranges from 0.1 to 114 mg/L and chloride varied from 2 to 35.5 mg/L in all water samples (Table 5.1). NO_3^- concentration ranges from 0.03 mg/L to 85.5 mg/L in all water samples. High amount of NO_3^- contents are observed in a shallow well (MM-9) with a concentration of 85.5 mg/l. The high nitrate is related to anthropogenic pollution. The area is mostly used for agricultural purposes which cause the leaching of fertilizer. Recently nitrate pollution from anthropogenic sources mostly affects unprotected shallow wells in the volcanic aquifer (Alemayehu et al., 2011; Ayenew, 2008; Haji et al., 2021; Sallis et al., 2001). The observed high content of NO_3^- indicates percolation of shallow groundwater into the deep aquifer (fig 5.2 F).

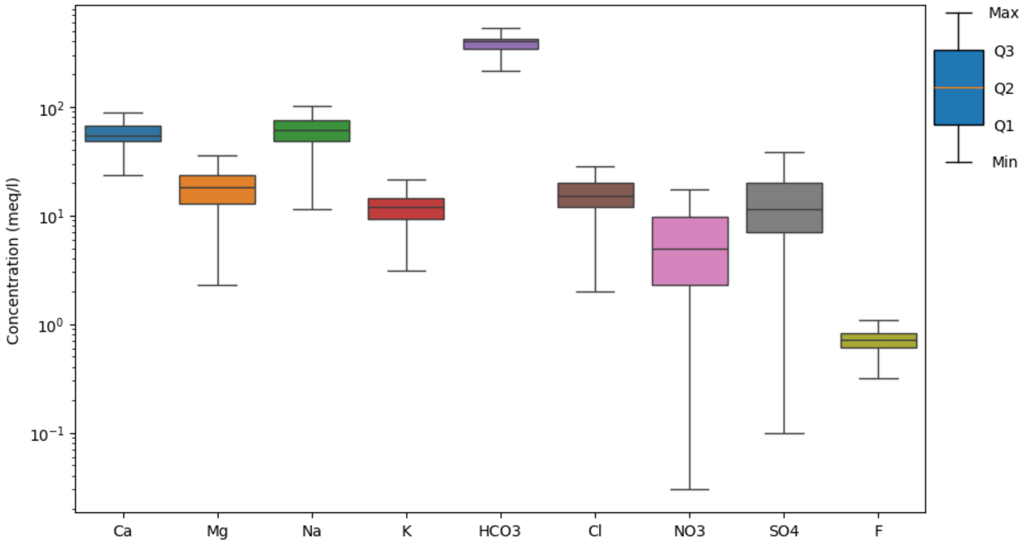


Figure 5: 3 Box and whisker showing variability of chemical composition of the groundwater. Q1, Q2 and Q3 represent the first, the second and the third quartile, respectively. Note: ionic concentration in meq/l.

5.4. Groundwater cluster and major ion signature

Hydro-chemical data were classified by hierarchical cluster analysis (HCA) in 12-dimensional space (TDS, pH, EC, Na, K, Mg, Ca, Cl, HCO_3^-, SO_4, F and NO_3^-) and the result is presented in dendrogram (Figure 5.4). Visual observation of the dendrogram was used to classify samples into clusters. Phenon line was drawn at linkage distance of about 1000 and the sample with a linkage lower than 1000 are grouped into the same clusters (Figure 5.4). Based on the phenon line, groundwater sample divided into four clusters, named G1-G4. The results of each cluster were clearly distinguishable in terms of hydrogeological and geological variables and classified according to increasing values of hydro-chemical variables (Table 5.4).

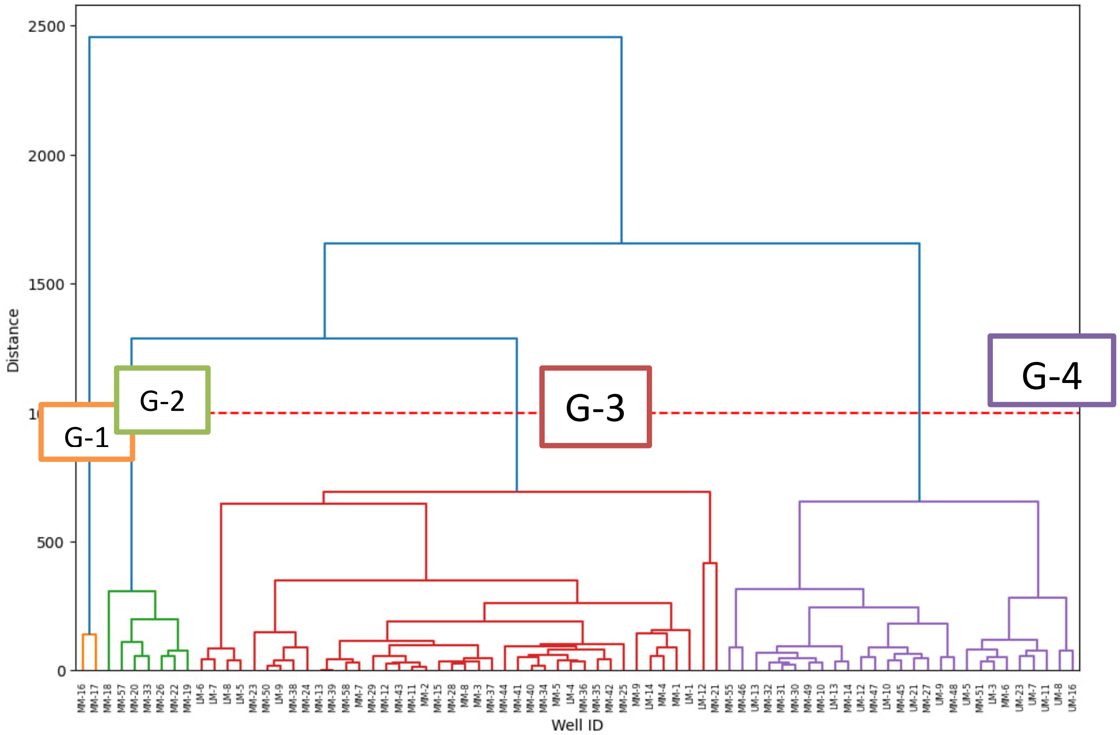


Figure 5: 4 cluster analyses (dendrogram)

Table 5: 2 Average hydro-chemical variables of the water groups

	TDS	EC	pH	Na	K	Ca	Mg	HCO3	Cl	NO3	SO4	F	Water types
Unit	mg/L	µS/cm		mg/L									
Group1	1045	1541	6.75	242	33.5	118.56	11.61	1000	31.49	5.3	84.83	0.89	Na-HCO3
Group2	630.71	986.86	6.99	118.43	26.93	62.79	21.92	571.71	19.4	6.19	38.45	0.78	Na-HCO3
Group3	445.59	714.05	7.31	70.33	12.51	54.36	18.26	401.01	18.78	8.33	18.78	0.77	Na-Ca-HCO3
Group4	329.03	552.33	7.44	42.18	9.17	54.1	17.1	334.49	10.12	6.75	8.44	0.68	Ca-Na-HCO3

To describe the characteristics of each cluster of samples, Table 5.2 presents the mean values of geochemical and physical data, including the chemical parameters used in the HCA. The mean values of the major ions were used to determine groundwater type for each cluster. The descriptive statistics indicate that the four clusters are geochemically distinct groups of samples (Table 5.2). The samples clustered in G1 are MM-16 and MM-17. The two samples points show high TDS and EC. This shows there is high concentration of dissolved minerals.

Both samples have high sodium contents with high bicarbonate. The high bicarbonate is from weathering of silicate. These wells likely share very specific characteristics that are different from all other wells. The first group of waters, group 1, has high salinity (mean EC = 1541 μS/cm) and abundance orders (meq/l) Na^{+}>Ca^{2+} > K^{+} Mg^{2+} and HCO_3 > $SO_2{}^{4}$> Cl > NO_3>F (table 5.2). These waters are classified as HCO3 -alkaline water type (Na-HCO_3). The water type 2 (group 2) is bicarbonate dominated anion and Na cation (Table 5:2).The electrical conductivity for this group is 986.86 μS/cm which is the characteristic of Na- HCO3 water. Seven samples were clustered in G2. The samples clustered in G3 were largest cluster in the center of the dendrogram (figure 5:4). The group contains 40 samples (31 samples from middle Modjo and 9 samples from lower Modjo). The group is with bicarbonate domination, but also it contains low concentrations of sulfate and chloride. The sodium and calcium are the dominant cations. The mean EC value is 714.05μS/cm which is the characteristic of blended water (Na-Ca-HCO3). From the four groups, it is the group with the highest value of nitrate (NO_3). High nitrate levels are often linked to the use of nitrogen-based fertilizers in agriculture (Cloutier et al., 2008). The water type 4 (group 4) contains 30 samples out of 79 samples (10 samples from upper Modjo, 17 samples from middle Modjo, 3 samples from lower Modjo). It is found with domination of bicarbonate anion and calcium and sodium cations (Table 5:2).The electrical conductivity for this group is 552.23μS/cm. It has the characteristic of blended water (Ca-Na- HCO3). Low TDS and EC indicate that the water is less mineralized (fewer dissolved salts).This suggests the groundwater heavily influenced by fresh, less mineralized recharge, such as rainwater infiltration. The groundwater may not have had enough time to dissolve significant minerals from the aquifer rocks (young water). Lower dissolved CO_2 levels can lead to higher pH. The low concentrations of ions suggest; the aquifer materials composed of less reactive rocks, such as quartz-rich sands, which do not dissolve easily to contribute ions. Some wells were located in an area close to recharge zones (e.g., areas where rainwater or surface water infiltrates quickly into the aquifer). The general overview of these groups is; as the flow of ground water is from the recharge area to discharge area its chemistry changing gradually. It's because of exchanging between cations.

Principal components analysis of groundwater chemical variables produced four components (Table 5.3). The first four components extracted have eigenvalues greater than 1, and account for

76.67% of the total variance in the dataset. The Varimax normalized rotation was applied to maximize the variance of the first four principal axes (Cloutier et al., 2008; Hsieh, 2001). Loadings, that represent the importance of the variables for the components, are in bold for values greater than 0.5 (Table 5.3).

Four components explain 76.67% of the variance of the original data set. Component 1 which is associated with the variables (TDS, EC, Na, K, Ca, HCO3−, Cl, and SO4,) explains 43.649% of the variance. Probably it shows the result of mineral water reactions in the area. Component 2 which is composed of the variables Ph., Mg, and Ca explains 11.976 % of the variance. In this factor Ca is loads in negative side. The negative loading suggests that Ca^{2+} is inversely correlated with variables or processes represented by the positive side of the same principal component. Factor 3 explains 10.661 % of the total variance and has high loading in the ions Mg, NO_3 and F. Factor 4 explains 10.391 % of the total variance and mainly represented with NO_3. It shows that, the area is associated with surface run-off nitrate fertilizer as the aquifer of the area is used for agricultural purpose.

Table 5: 3 : Principal component Analysis for each parameter

		Component			
	Communality	1	2	3	4
TDS	0.855	**0.921**	-0.048	0.032	-0.059
EC	0.951	**0.964**	0.116	0.081	0.044
pH	0.757	-0.361	**0.651**	-0.175	0.415
Na	0.903	**0.905**	0.204	-0.168	-0.119
K	0.659	**0.784**	-0.135	-0.061	0.151
Ca	0.635	**0.493**	**-0.506**	0.219	0.296
Mg	0.805	0.048	**0.686**	**0.576**	-0.017
F	0.646	0.172	0.077	**-0.697**	0.446
Cl	0.485	**0.609**	0.275	0.169	0.098
NO3	0.848	-0.044	-0.259	**0.544**	**0.695**
HCO3	0.853	**0.911**	0.079	0.121	-0.044
SO4	0.730	**0.738**	0.054	-0.238	0.355
Explained Variance		5.238	1.437	1.279	1.247
Explained Variance%		43.649	11.976	10.661	10.391
Cumulative% of variance		43.649	55.626	66.286	76.678

Figure 5.4 summarizes this information by showing the position of the loadings of chemical parameters in the plane defined by the axes of components 1 and 2.

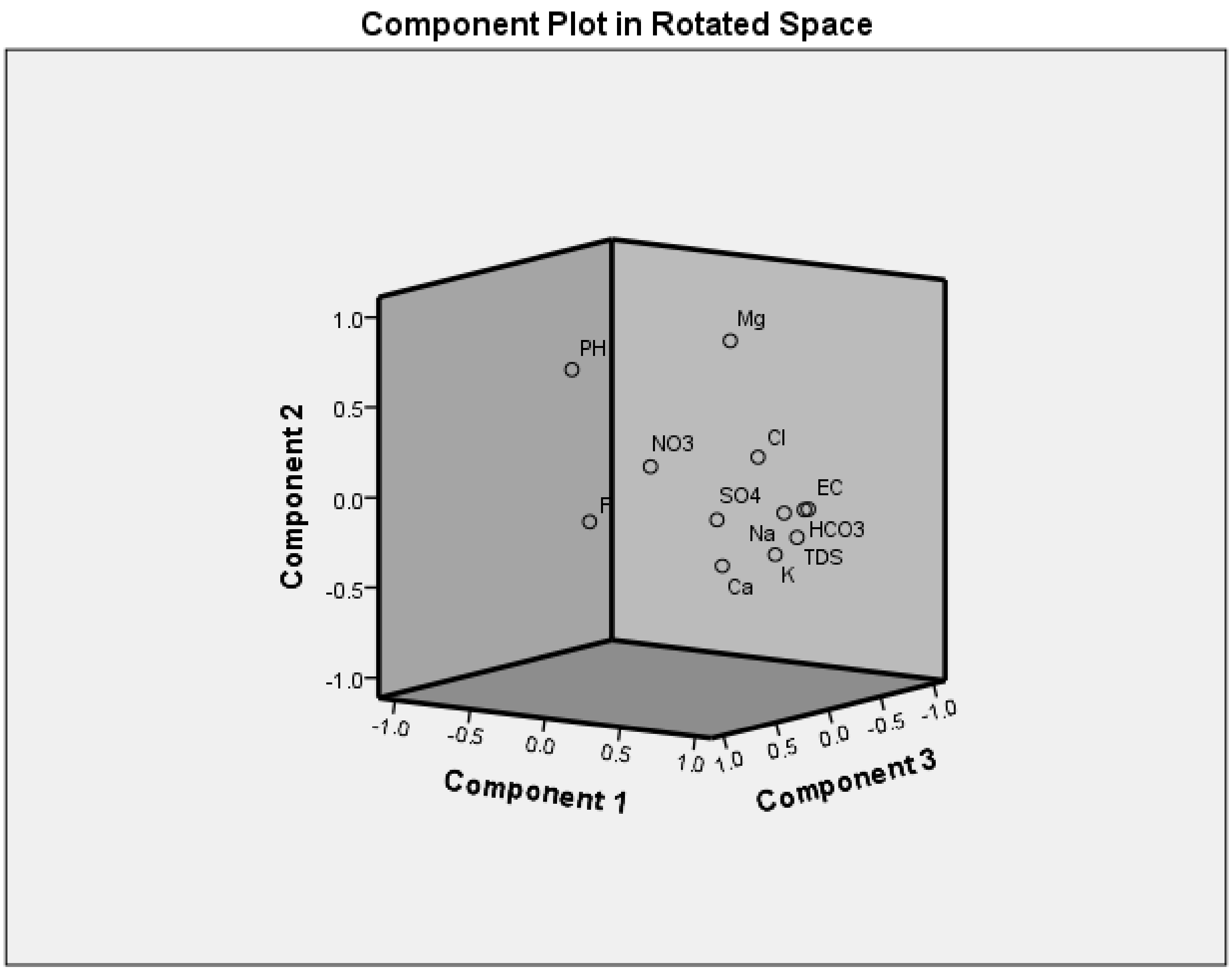


Figure 5: 5 Component plot in rotated space

This figure shows (fig. 5:5), pH behaves differently compared to the ionic composition and other water quality parameters (Cloutier et al., 2008). It indicates areas influenced by specific chemical or geochemical processes. Cluster of TDS, EC, HCO_3, Ca, Mg, Cl, SO_4, Na, K are closely grouped, indicating they are strongly correlated. These parameters are likely driven by mineral dissolution and general water ionic strength. TDS and EC, which measure overall ionic content, naturally correlate with major ions like Mg^{2+}, and Cl^{-}. Nitrate (NO_3) and fluoride (F) are positioned further away from the main ion group.

5.5. Fluoride Concentration

According to table 5.1, the concentration of fluoride in the study area ranges from 0.07 to 1.9. It is found that water samples taken from upper Modjo catchment have low mean fluoride value (0.67 mg/L), whereas water samples taken from middle Modjo catchment have a mean fluoride value of 0.68 mg/L. The water samples taken from lower Modjo catchment shows a mean fluoride value of 1.09 mg/L. Thus, fluoride content in groundwater grows from high lands towards the rift floor. The fluoride enrichment is caused by geological events involving a cation exchange reaction in groundwater as a result of the reaction process's removal of Ca^{2+} from solution (Furi et al., 2011). Volcanic rocks, such as basalt, rhyolite, and pumice, are rich in fluoride-bearing minerals like fluorite (CaF_2) and apatite. When groundwater interacts with these rocks, fluoride is released through weathering and dissolution processes. As the water travels from highland to lowland regions, its longer contact with fluoride-rich rocks leads to increased concentrations in the lowlands (Malago, 2017).

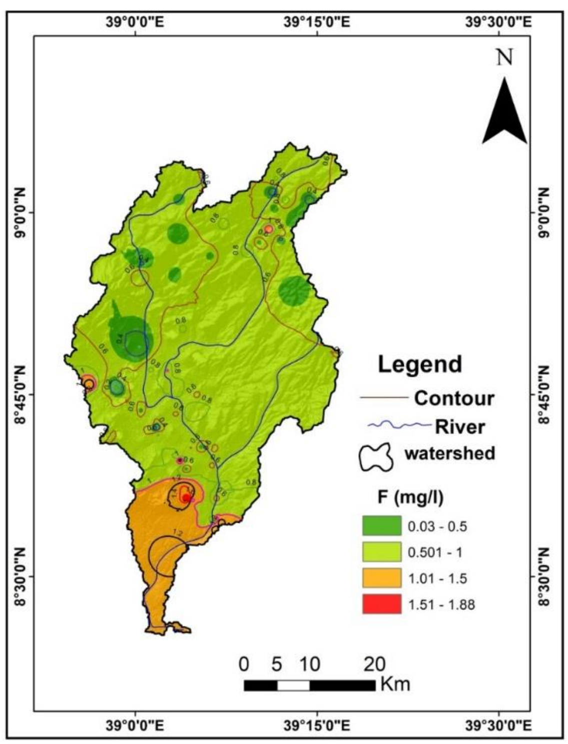


Figure 5: 6 Spatial distribution of fluoride

5.6. Hydro-geochemical facies

The goal of studying hydro-chemical facies is to understand the chemical makeup of water that is connected to the lithological and hydrological characteristics of aquifers(Chadha, 1999). The chemical makeup of water, including the concentrations of main and minor ions, defines hydro-geochemical facies. Groundwater samples from the Modjo River basin show a clear spatial hydro-chemical distribution. For this plot meq/L unit was used.

One of the most popular and useful graphical methods for displaying water chemistry data to aid in comprehending the characteristics and fluctuations of the dissolved ions in water is the Piper diagram (Piper, 1944). Groundwater samples that were collected from the upper Modjo area are predominantly Ca -Na -HCO_3 type. The reason is that, the area is closer to recharge zones where fresh water infiltrates from precipitation or surface water. Groundwater samples that were collected from the middle Modjo and lower Modjo part are predominantly Na-HCO3 type.

As groundwater flows from the upper to middle and lower parts, it spends more time in contact with rocks and sediments. During this longer residence time, cation exchange becomes a dominant process. In cation exchange, Ca^{2+} and Mg^{2+} ions in the water are replaced by Na^{+} ions from clay minerals or other subsurface materials. This shifts the hydro-chemical facies to Na-HCO_3 type. In the area, it is observed that hydro-chemical facies are dominated by Na-Ca-HCO_3. The Piper diagram in figure below (fig 5.7) indicates that various water types exist within the groundwater at Modjo River Basin based on the major ions present.

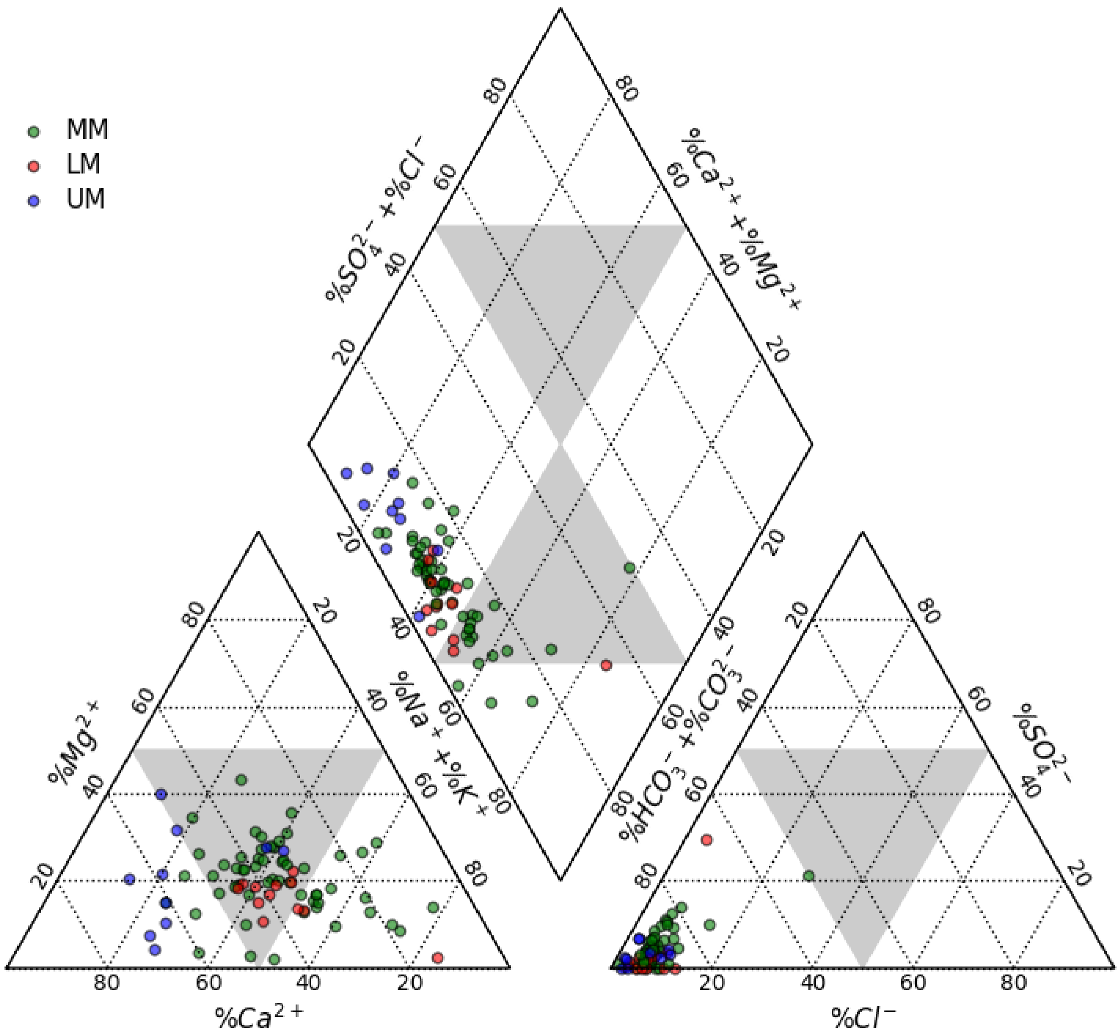


Figure 5:7 piper diagram representing hydro-chemical facies

Hydro-geochemical facies evolution diagram (HFE-D), a multi-rectangular diagram, to study the processes of sea water freshening and intrusion (Giménez-Forcada et al., 2010). HFE-D has a total of 16 hydro-chemical facies, which are determined by taking into account the mill equivalent percentages of four important cations ($Ca^{2+,}$ Mg^{2+}, Na^{+}, and K^{+}) and four major anions (SO^{2}_{4}, Cl^{-}, CO3, and HCO_3) and their correlations.

The hydro geo-chemical facies plot (fig 5:8) illustrates the relationships between different ion concentrations in groundwater samples, with the x-axis representing the combined concentrations of sodium (Na^+) and potassium (K+) ions, while the y-axis shows the combined concentrations of bicarbonate (HCO_3^-) and sulfate (SO_4^2) ions. Within the plot, distinct zones are identified, including the Freshwater (FW) zone characterized by lower concentrations of Na^+ and K^+, indicative of typical freshwater conditions. Additionally, an Intrusion Zone suggests the mixing of freshwater with saline water, often due to processes like seawater intrusion or contamination. But nothing sample point fall in the region.

The diagonal trend line indicates that as the proportion of bicarbonate decreases, the proportion of sodium and potassium increases, highlighting the transition from freshwater to saline water. The curve represents shifts in hydro-chemical facies, demonstrating how groundwater chemistry evolves through various processes, such as mixing and geochemical reactions. The colored data points on the plot represent different groundwater samples, with their distribution indicating respective hydro-chemical characteristics. Samples clustered in the FW zone reflect typical freshwater chemistry. Overall, this plot effectively visualizes variations in groundwater chemistry based on ion concentrations, aiding in the identification of dominant processes that influence water quality, such as freshwater mixing. According this plot; the area's domination water type is Na-HCO3 to Ca-Na-HCO3 to Ca-HCO3. Most of the samples of the study undergo Na-Ca- HCO3.

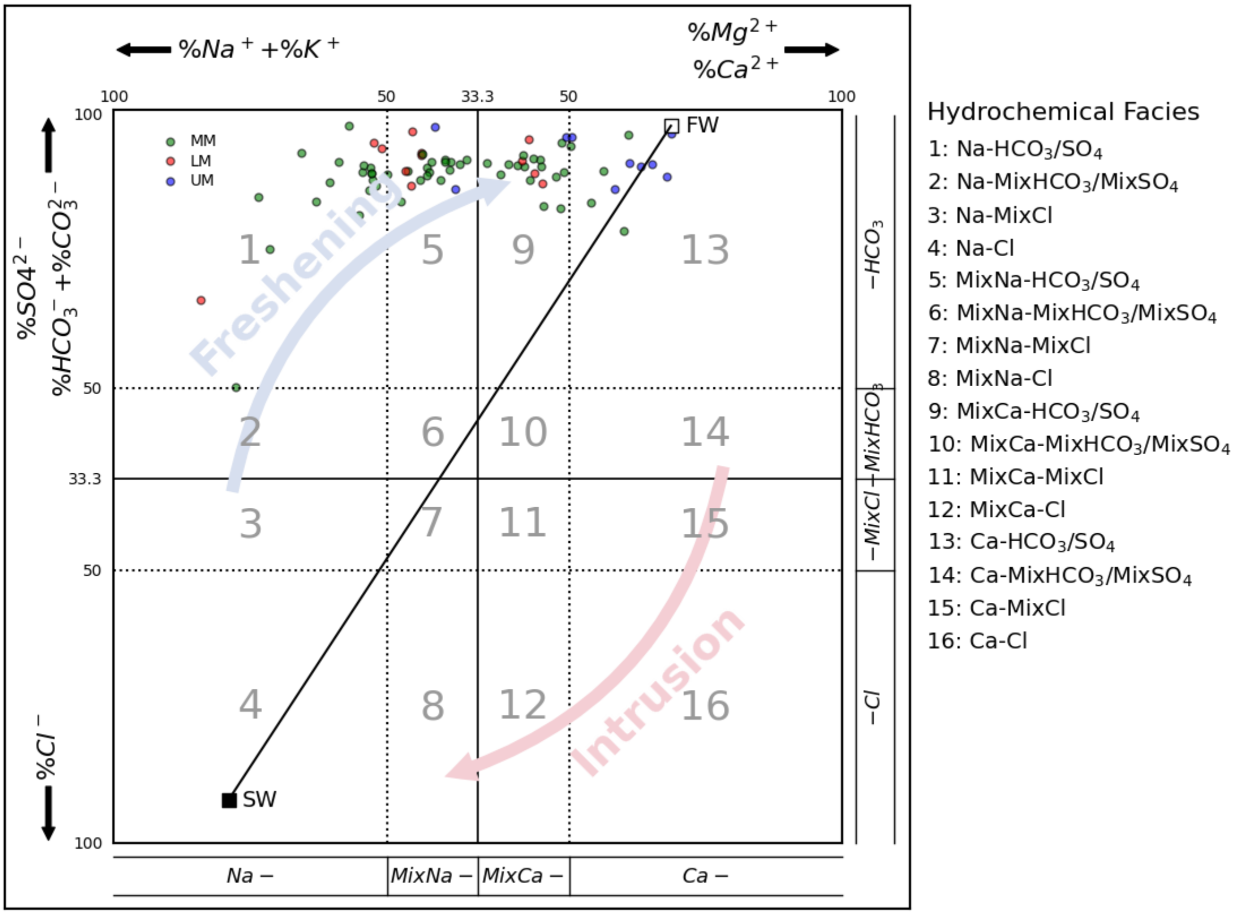


Figure 5: 8 Hydro-geochemical facies evolution diagram.

5.6. Geochemical process controlling groundwater chemistry

Groundwater chemistry is largely a function of mineral composition, the formation through which it flows due to rock–water interaction. Different geochemical process such as evaporation and concentration, dissolution/precipitation, ion exchange processes, hydrolysis, oxidation and reduction can change the chemical composition of groundwater (Elango & Kannan, 2007). The rock–water interaction is the major process because solid phases are the primary sources and sinks of dissolved constituents of groundwater. The hydrolysis of silicate rocks is a key geochemical process controlling the major ions chemistry of the groundwater, especially in fractured rock aquifers. The resulting concentrations of major ions of groundwater can be used to identify the intensity of rock–water interaction and chemical reactions.

Silicate hydrolysis resulting to the release of cations like Ca^{2+}, Mg^{2+}, K^+ and Na^+ and the balancing bicarbonate ion into the groundwater. The general reaction of silicate rocks with carbonic acid can be written as:

$$(Na, K, M\quad, Ca)\ silicate + H_2CO_3 = H4SO_4 + Na + K + Mg + Ca + soild\ prouct$$

Hence, knowledge on rock–water interaction that control groundwater chemical evolution will lead to improved understanding of hydro-geochemical characteristics of an aquifer. This would contribute in the effective management and utilization of groundwater resources.

The aquifer is mainly volcanic rock in study area where the silicate mineral is the main component forming rock. As the silicate hydrolysis in the study area is controlled by the uptake of CO_2 (Darling et al., 1996; Haji et al., 2021), the bicarbonate content is related to concentrations of dissolved cations according to the reactions given below as an example. The incongruent reaction of anorthite and albite in the presence of CO2 can yield kaolinite and a Ca^{2+}– and Na^+–HCO_3^- solution.

$$CaAl_2Si_2O_8 + 3H_2O + 2CO_2 \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^-$$

$$2NaAlSi_3O_8 + 3H_2O + 2CO_2 \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4$$

The relationship maintained between the concentrations of major ions can help to understood and illustrate the geochemical process. The sum of cationic species of Ca^{2+}, Mg^{2+}, K^+ and Na^+ was plotted against the HCO_3^- anion and linearly correlated with a coefficient of 0.8859, which is very close to 1. This value shows that, there is strong correlation between them. Bicarbonate has high contribution for total cation. When carbonate weathering dominates, most of the total cations are derived from Ca^{2+} and Mg^{2+} due to reaction. This leads to a strong correlation between total cations and bicarbonate. This correlation of cationic species, [Ca^{2+} + K^+ + Mg^{2+} +Na^+] and [HCO_3^-], suggesting that the cations are balanced mainly by the bicarbonate anion (Figure 5.9) and confirm that the silicate hydrolysis is the most governing hydro-chemical process.

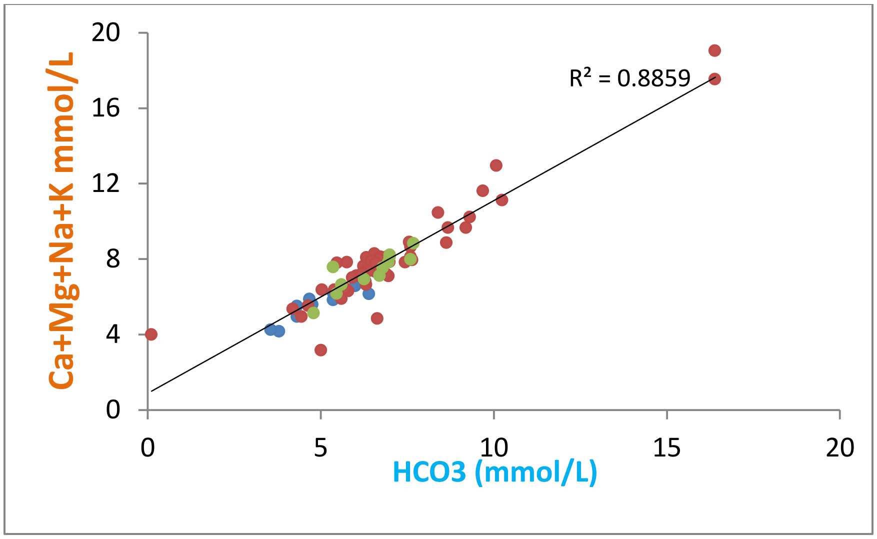


Figure 5: 9 Concentration of HCO3 to total cations

Calcium (Ca2+) and magnesium (Mg2+) are often dominant alkaline earth cations in natural waters, and their proportion relative to the total cationic charge which helps to identify key influences on groundwater chemistry and classify water types. The (Ca^{2+}+Mg^{2+}) versus total cation (TZ^{+}) plot was used to estimate the contribution of ions from silicate weathering (figure 5.10) and resulted with average equilibrium ratio of 50% indicating the contribution of Ca and Mg to total cations is 50%. The maximum values, 9.154, 5.72 were observed in the well (MM-17, MM-50). The high values indicate that the aquifer is mainly composed of silicate lithologic unit.

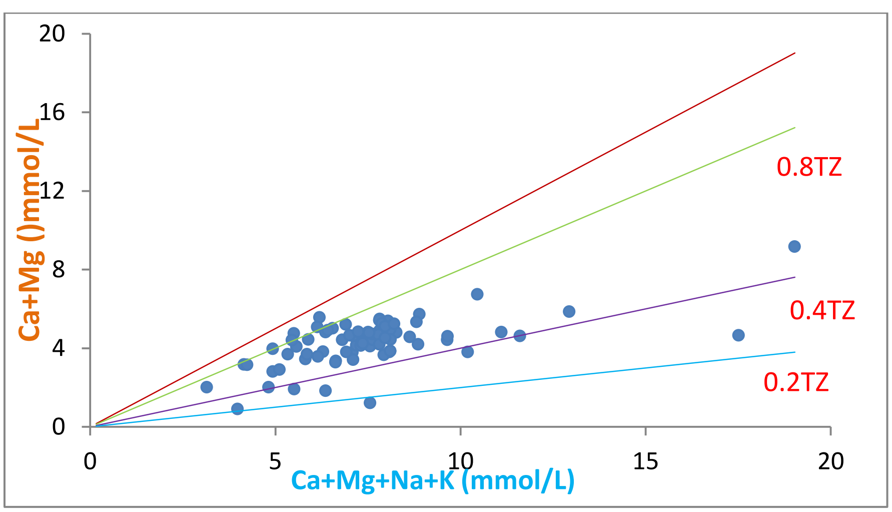


Figure 5: 10: Concertation of Ca and Mg to total cation

The plot of (Na^{+}+K^{+}) vs TZ^{+}; was used as an index to estimate the contribution of cations from silicate hydrolysis. The scatter plot between Na^{+} + K^{+} and total cations was constructed in order to estimate the contribution of sodium and potassium to the water. The scatter plot gives an estimate the Na^{+} + K^{+} value is range from 10% to 70%. It shows contribution of Na+ Mg to total cation is minimum of 10 % and maximum of 70%. This shows, it has 40% of the total cations contribution (Figure 5.11). From 79 samples, only four samples have contribution of more than 70% (MM-16, MM-1, MM-21, and LM-1). The rest samples have the contribution 10% to 70%. Hence, the relationship shows the silicate hydrolysis is the main geochemical process controlling the groundwater chemistry, which adds mainly sodium ions to the groundwater.

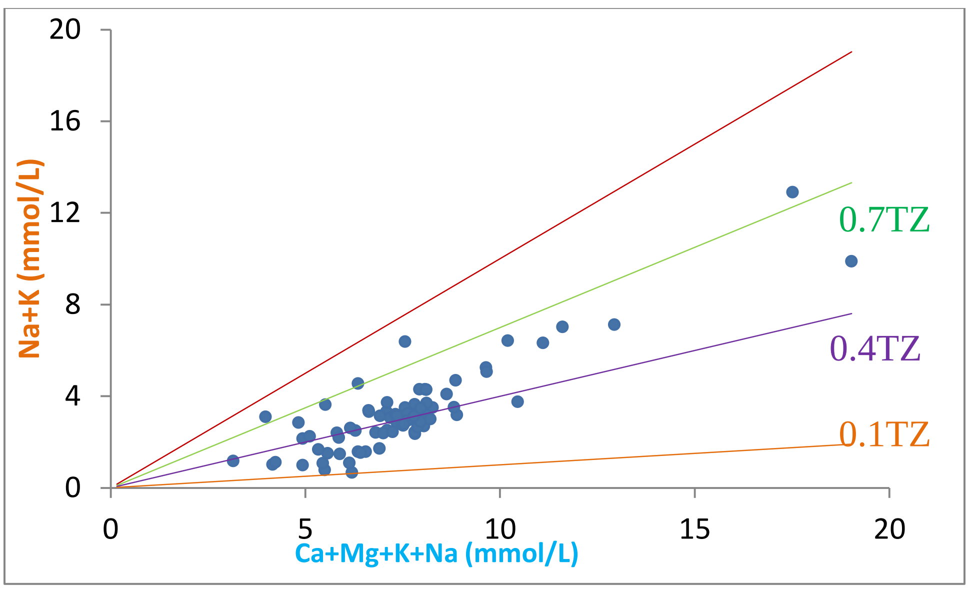


Figure 5: 11: Concertation of Na and potassium to total cation

Gibbs examined the mechanisms controlling the development of surface water chemistry using a vast array of rain, river, lake, and ocean water samples that were gathered all around the world. The three main regulating mechanisms are evaporation, precipitation, and water-rock interaction (Yang et al., 2022). Using a Gibbs plot, the relationship between the processes governing the chemical variation and the composition of water has been determined. With the Gibbs diagram, the mechanisms governing the composition of groundwater can be evaluated.

The Gibbs diagrams in figure below shows that the primary factor influencing the water composition at all sites is rock weathering. On the other hand, it is evident that shallow groundwater sites group significantly closer, while deep groundwater locations obviously map away from surface water. This indicates that, due to rock weathering, rock dominance extends towards lower TDS concentrations at higher Na+/(Na+Ca2+) ratios the groundwater flow regime.

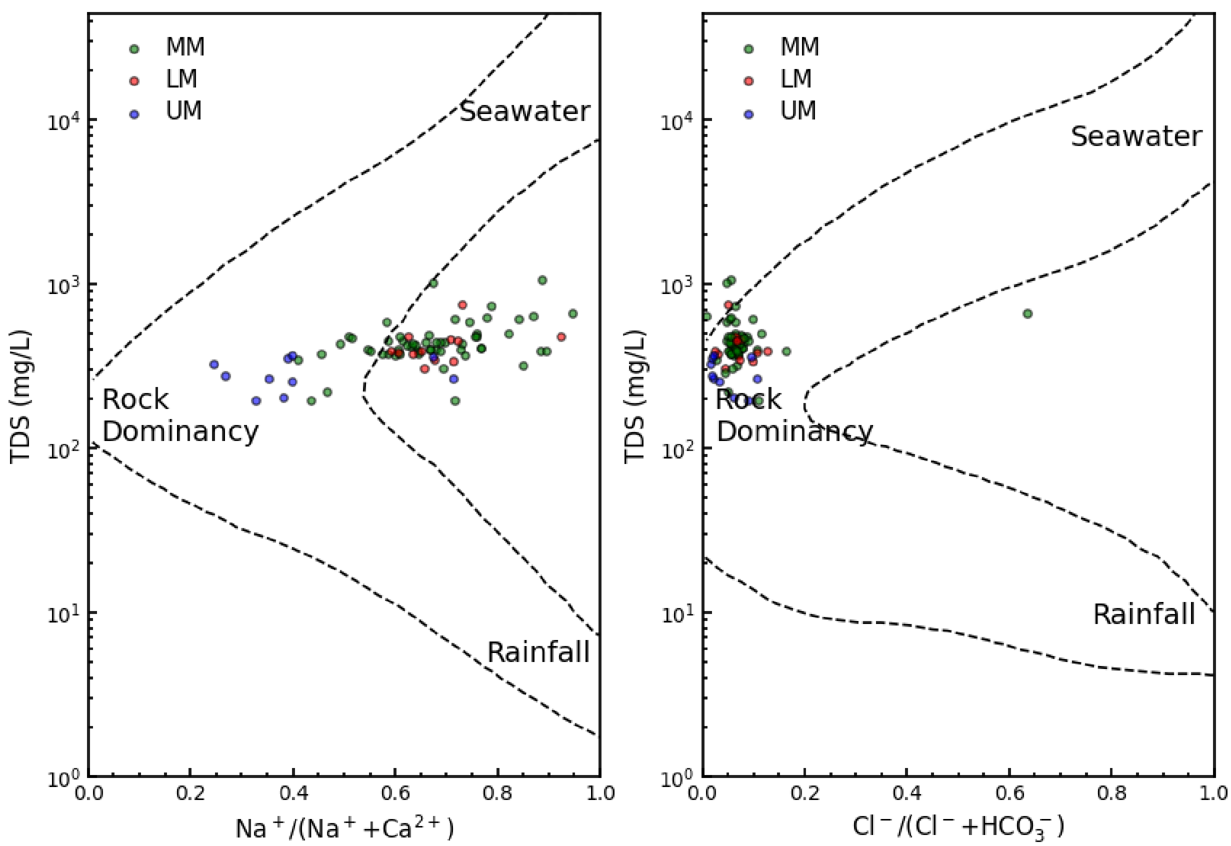


Figure 5: 12: Gibbs diagram of TDS concentrations vs ion

Gaillardet al. (1999) developed a diagram that are helpful in identifying different types of water-rock interactions for surface water geochemistry (Gaillardet et al., 1999)Particularly, the diagram can help to distinguish evaporate dissolution, silicate weathering, and carbonate dissolution that govern the water-rock interactions:. The diagram was used for this study to investigate the main geochemical processes that govern groundwater chemistry of the study area.

The plot below (Figure 5.13) displays the relationship between the concentrations of different chemical species in water samples and, shows that most of the water sample falls in the region of silicate hydrolysis. Hence, silicate hydrolysis is one of the most governing hydro-geochemical processes and also in agreement shown by the relationship between total cation and bicarbonate (see Figure 5.9).

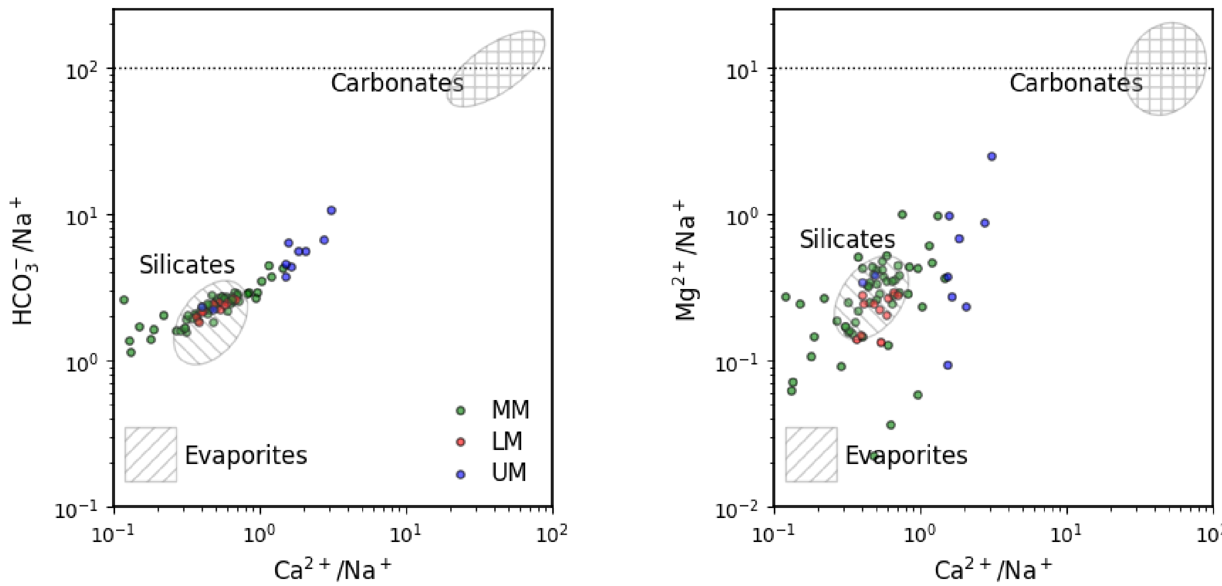


Figure 5: 13: Gaillardet diagram for carbonates, silicates, and evaporates

Chadha created a schematic that can be used to categorize natural water and recognize hydro-chemical processes (Chadha D., 1999). The Chadha diagram is helpful in differentiating between the types of water that arise from different hydro-geologic processes, like mixing and cation exchange in seawater. Using a Chadha plot, the various hydro-chemical reactions in groundwater were identified. The four quadrants of the Chadha plot, which include seawater (Na-Cl), base ion exchange water ($Na\text{-}HCO_3$), recharge water (Ca-Mg-HCO3), and reverse ion exchange water (Ca-Mg-Cl), explained the major hydro-chemical processes.

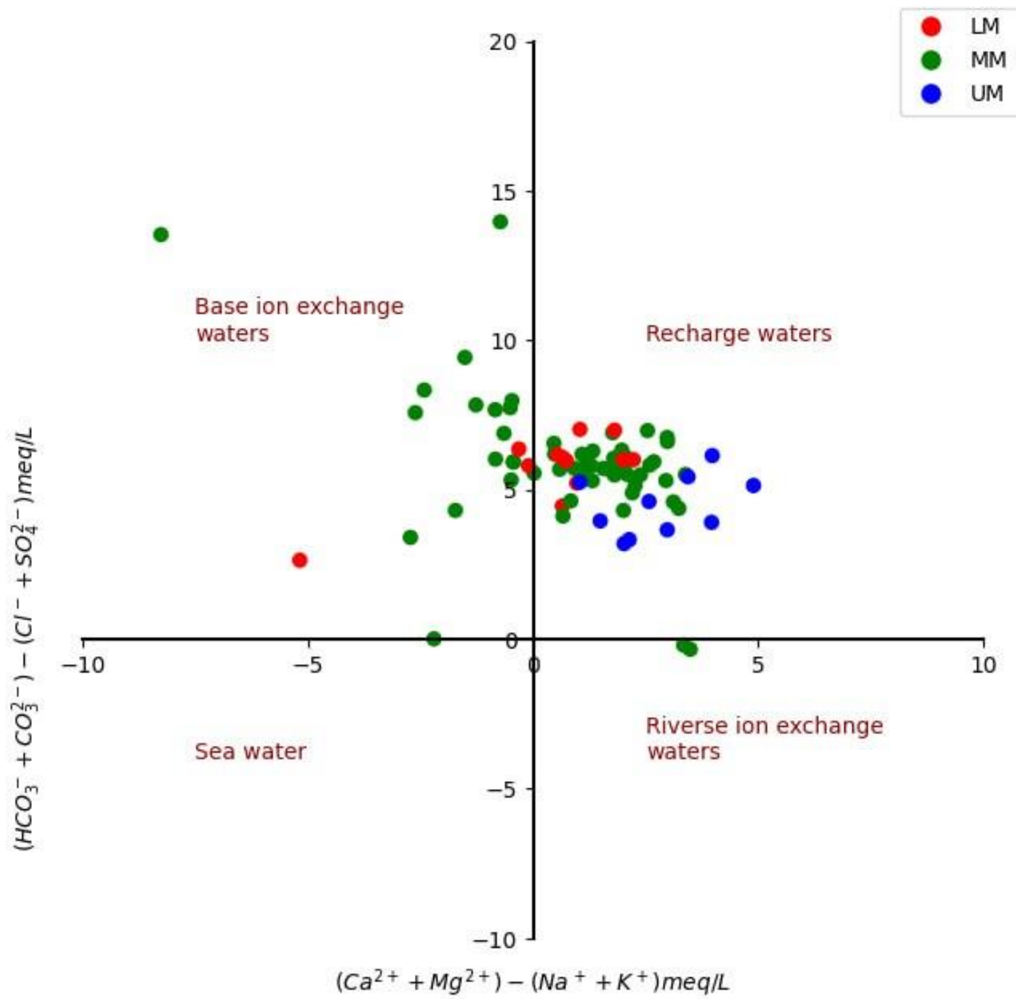


Figure 5: 14: Chadha plot of the major ions

The plot shows (Figure 5:14) the distribution of various groundwater samples based on their major ion chemistry, specifically the $(Ca^{2+} + Mg^{2+}) - (Na^+ + K^+)$ and $HCO_3^- + CO_3^{2-} - (SO_4^{2-} + Cl^-)$ ratios. The different geochemical processes are identified, including base ion exchange waters and recharge waters. The distribution of the data points on the plot suggests a clear geochemical evolution trend, with the samples transitioning from recharge waters to base ion exchange waters. This evolution likely reflects the progressive water-rock interactions, and ion exchange processes occurring within the groundwater system. The data points show distinct clustering, with the majority of the samples concentrated in the base ion exchange and recharge waters regions.

To evaluate the degree of base exchange during weathering in the study area, chloro-alkaline indices were utilized using the equations below, as ion exchange was the primary hydro-geochemical process. The chloro-alkaline index is used to evaluate the ion exchange processes in water, particularly focusing on the balance between cations.

$$CAI1 = [Cl - (Na + K)/Cl] \quad \text{…………………………….…….. (1)}$$

$$CAI2 = [Cl - (Na + K)/(SO4+HCO3+NO3)] \quad \text{………………..(2)}$$

It provides an indication of the ion exchange processes in the groundwater.

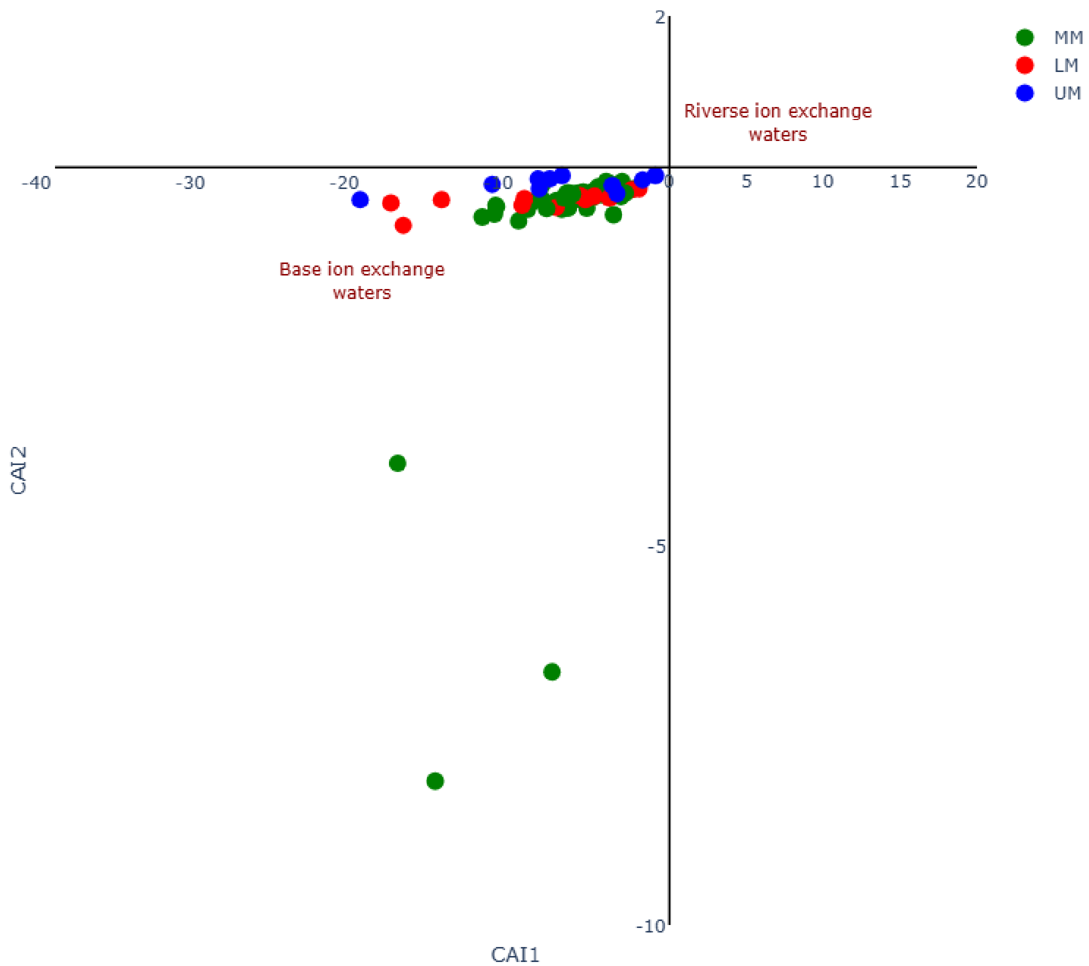


Figure 5: 15: Chloro-alkaline plots illustrated with ionic relationships

According to the above plot (fig. 5.15), positive CAI values indicate base ion exchange, where Ca^{2+} and Mg^{2+} ions in the groundwater are exchanged for Na^{+} and K^{+} ions from the rock/soil matrix. Negative CAI values indicate base ion exchange, where Na+ and K^{+} ions are exchanged for Ca^{2+} and Mg^{2+} ions. The distribution of the data points on the plot shows a clear trend from positive to negative CAI values. This suggests that the groundwater samples are undergoing base ion exchange processes.

The data points are distributed across the plot, with some clustering observed, especially in the positive CAI region. A few outliers with more extreme CAI values are also present, which may indicate localized geochemical processes or the influence of additional water sources.

The overall trend from positive to negative CAI values reflects the progressive geochemical evolution of the groundwater system. This evolution is driven by factors such as water-rock interactions, mineral dissolution/precipitation, mixing with different water sources, or changes in

CHAPTER SIX

CONCLUSION AND RECOMMANDATION

6.1 CONCLUSION

Groundwater in a volcanic aquifer of Modjo River catchment that situated in the Upper Awash River Basin; where the composition and evolution of groundwater is barely known. Thus, a sound understanding of the spatial variation of groundwater chemistry, its evolution and controlling mechanism is therefore required for an adequate development and management of groundwater resources in the basin. T To investigate this issue major ion chemistry and multivariate statistical analysis were applied.

Major ions in groundwater reveal its origin with cations like potassium (K^+), sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) sourced from mineral weathering and dissolution. Anions such as bicarbonate (HCO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), and fluoride (F^-) originate from carbonate rocks, fertilizers, and natural minerals. In the study area, sodium is the dominant cation, followed by calcium, with high bicarbonate levels attributed to volcanic gas emissions and hydrothermal processes. Sulfate concentrations range from 0.1 to 114 mg/L, chloride from 2 to 35.5 mg/L, and nitrate from 0.03 to 85.5 mg/L. Fluoride levels in the study area range from 0.07 to 1.9 mg/L, showing an increase from highlands to the rift floor.This rise in fluoride concentration is linked to geological processes, especially cation exchange that removes calcium (Ca^{2+}) from groundwater. Fluoride is released from volcanic rocks rich in minerals like fluorite (CaF_2) and apatite. The study of hydro-chemical facies examines the chemical composition of groundwater in relation to aquifer characteristics. The Piper diagram reveals that the area has predominantly *Ca-HCO3 to Ca-Na-HCO3 to Na- Ca-HCO3* type water due to nearby recharge zones.

Groundwater chemistry is influenced by the mineral composition of surrounding rocks and various geochemical processes, including evaporation, dissolution, ion exchange, and hydrolysis. A significant process is silicate hydrolysis, which releases cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and bicarbonate into the groundwater, reflecting the intensity of rock-water interactions. In volcanic rock aquifers, the uptake of CO_2 plays a crucial role in silicate hydrolysis, leading to the production of bicarbonate solutions. There is a strong correlation between major ion concentrations, especially between cations and bicarbonate, indicating that bicarbonate effectively balances these cations.

Gibbs plots indicate that rock weathering is the primary factor influencing groundwater composition. The Gaillardet diagram confirms that silicate hydrolysis is a dominant geochemical process, while the Chadha diagram, showing transition from recharge waters to base ion exchange waters, highlighting the role of water-rock interactions. Chloro-alkaline indices assess ion exchange processes, showing a spectrum from positive values (indicating base ion exchange) to negative values (indicating reverse ion exchange). This trend reflects the progressive geochemical evolution of the groundwater system, emphasizing the importance of understanding these interactions for effective groundwater management and resource utilization

These findings provide valuable insights into the geochemical processes influencing groundwater quality in the basin, offering a foundation for understanding its evolution and underlying dynamics.

6.2 Recommendation

To eradicate obstacles happened in the thesis; various recommendations might be made to rectify this issue. First, data gathering activities should be in critical way. This may entail working with relevant government agencies, research institutes, or local stakeholders to collect any existing hydrogeological, water quality, or other relevant data for the Modjo River Basin. A more intense field campaign might also be done to collect a comprehensive collection of groundwater samples and measurements, such as water levels, flow rates, and a broader range of physicochemical characteristics.

Secondly, the sampling design should be optimized to ensure an even spatial distribution of sampling points across the basin, with a higher density in areas of particular interest or concern. Additionally, a regular monitoring schedule should be established to collect groundwater data (e.g., quarterly, bi-annually) to assess temporal trends). By implementing these recommendations, the thesis can better address the overall hydrogeological and hydro-geochemical evolution of the study area.

References

Ahmed, A., & Clark, I. (2016). Groundwater flow and geochemical evolution in the Central

Flinders Ranges, South Australia. *Science of the Total Environment*, *572*, 837–851.

Al Haj, R., Merheb, M., Halwani, J., & Ouddane, B. (2023). Hydrogeochemical characteristics of groundwater in the Mediterranean region: A meta-analysis. *Physics and Chemistry of the Earth, Parts A/B/C*, *129*, 103351. https://doi.org/10.1016/J.PCE.2022.103351

Alemayehu, T., Leis, A., Eisenhauer, A., & Dietzel, M. (2011). Multi-proxy approach (2H/H, 18O/16O, 13C/12C and 87Sr/86Sr) for the evolution of carbonate-rich groundwater in basalt dominated aquifer of Axum area, northern Ethiopia. *Geochemistry*, *71*(2), 177–187.

Alemu, M. G., Wubneh, M. A., & Worku, T. A. (2022). Impact of climate change on hydrological response of Mojo river catchment, Awash river basin, Ethiopia. *Geocarto International*, 2152497.

Appelo, C. A. J., & Postma, D. (2004). *Geochemistry, groundwater and pollution*. CRC press.

Appelo, C. A. J., & Postma, D. (2005). Geochemistry, groundwater and pollution. 2-nd edition. *AA Balkema, Leiden, 649*.

Ayenew, T. (2005). Major ions composition of the groundwater and surface water systems and their geological and geochemical controls in the Ethiopian volcanic terrain. *SINET: Ethiopian Journal of Science, 28*(2), 171–188.

Ayenew, T. (2008). The distribution and hydrogeological controls of fluoride in the groundwater of central Ethiopian rift and adjacent highlands. *Environmental Geology*, *54*, 1313–1324.

Ayub, S. A., Tsegab, H., Rahmani, O., & Beiranvand Pour, A. (2020). Potential for CO2 mineral carbonation in the paleogene segamat basalt of Malaysia. *Minerals*, *10*(12), 1045.

Baker, L. L., & Neill, O. K. (2017). Geochemistry and mineralogy of a saprolite developed on Columbia River Basalt: Secondary clay formation, element leaching, and mass balance during weathering. *American Mineralogist*, *102*(8), 1632–1645.

Baptista, L. (2021). *Using Python and Google Colab to Teach Physical Chemistry During Pandemic*.

Basabe, P., & Bedir, G. (2007). No 主観的健康感を中心とした在宅高齢者における 健康関

連指標に関する共分散構造分析Title. *Combustion Science and Technology*, *21*(5–6), 508–516. https://doi.org/10.1080/00102208008946937

Belkhiri, L., Boudoukha, A., Mouni, L., & Baouz, T. (2010). Application of multivariate statistical methods and inverse geochemical modeling for characterization of groundwater—a case study: Ain Azel plain (Algeria). *Geoderma*, *159*(3–4), 390–398.

Belkhiri, L., Mouni, L., & Boudoukha, A. (2012a). Geochemical evolution of groundwater in an alluvial aquifer: Case of El Eulma aquifer, East Algeria. *Journal of African Earth Sciences*, *66*, 46–55.

Belkhiri, L., Mouni, L., & Boudoukha, A. (2012b). Journal of African Earth Sciences Geochemical evolution of groundwater in an alluvial aquifer : Case of El Eulma. *Journal of African Earth Sciences*, *66–67*, 46–55. https://doi.org/10.1016/j.jafrearsci.2012.03.001

Berehanu, B. (2007). *Impact of Industries and Urbanization on Water Resource in Mojo River Catchment*. Addis Ababa University.

Bhowmick, A., Yate, T. A., Shanka, A. S., Sandhar, B. S., Chaturvedi, S. K., & Ojha, J. R. (2023). Delineation of Ground Water Prospect Zones of Mojo Watershed, Ethiopia, East Africa, Using GIS, Remote Sensing and Analytical Hierarchy Process. *Journal of the Indian Society of Remote Sensing*, *51*(11), 2265–2283. https://doi.org/10.1007/S12524-023-01761-6/METRICS

Birhanu, B., Kebede, S., Charles, K., Taye, M., Atlaw, A., & Birhane, M. (2021). Impact of natural and anthropogenic stresses on surface and groundwater supply sources of the upper Awash sub-basin, Central Ethiopia. *Frontiers in Earth Science*, *9*, 656726.

Bisong, E., & Bisong, E. (2019). Google colaboratory. *Building Machine Learning and Deep Learning Models on Google Cloud Platform: A Comprehensive Guide for Beginners*, 59–64.

Blake, S., Henry, T., Murray, J., Flood, R., Muller, M. R., Jones, A. G., & Rath, V. (2016). Compositional multivariate statistical analysis of thermal groundwater provenance: A hydrogeochemical case study from Ireland. *Applied Geochemistry*, *75*, 171–188.

https://doi.org/10.1016/j.apgeochem.2016.05.008

Catania, S. (2022). *Hydrogeochemical evolution and quality assessment of groundwater within a basalt aquifer system, Tamborine Mountain, Queensland*.

Chadha D. (1999). Proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrogeology Journal*, *7*(5), 431–439.

Chadha, D. K. (1999). A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrogeology Journal*, *7*, 431–439.

Chebotarev, I. I. (1955). Metamorphism of natural waters in the crust of weathering—1. *Geochimica et Cosmochimica Acta*, *8*(1–2), 22–48.

Chorley, R. J. (2019). The role of water in rock disintegration. In *introduction to Fluvial Processes* (pp. 53–73). Routledge.

Cloutier, V., Lefebvre, R., Therrien, R., & Savard, M. M. (2008). Multivariate statistical analysis of geochemical data as indicative of the hydrogeochemical evolution of groundwater in a sedimentary rock aquifer system. *Journal of Hydrology*, *353*(3–4), 294–313.

Craswell, E. (2021). Fertilizers and nitrate pollution of surface and ground water: an increasingly pervasive global problem. *SN Applied Sciences*, *3*(4), 518.

Dalecha, N. B. (2021). *Groundwater quality evaluation for irrigation, Modjo River catchment, a wash basin, Central Ethiopia*.

Darling, W. G., Gizaw, B., & Arusei, M. K. (1996). Lake-groundwater relationships and fluid-rock interaction in the East African Rift Valley: isotopic evidence. *Journal of African Earth Sciences*, *22*(4), 423–431.

Dechasa, T. (1999). Water balance and effect of irrigated agriculture on groundwater quality in Wonji area/Ethiopian Rift Valley. *Unpublished MSc Thesis, Addis Ababa University, Addis Ababa, Ethiopia*.

Demlie, M., Wohnlich, S., Gizaw, B., & Stichler, W. (2007). Groundwater recharge in the Akaki catchment, central Ethiopia: evidence from environmental isotopes (δ18O, δ2H and 3H) and chloride mass balance. *Hydrological Processes: An International Journal*, *21*(6), 807–818.

Desissa, D. (2016). *SCHOOL OF GRADUATE STUDIES ADDIS ABABA INSTITUTE OF TECHNOLOGY QUALITY ASSESSMENT OF RURAL DRINKING WATER SUPPLY SCHEMES FROM SOURCE TO -POINT OF- USE . (A CASE STUDY OF ADA " A WOR EDA , IN OROMIA REGIONAL STATE OF ETHIOPIA). A Report Submitted to the* .

Devaraj, N., Chidambaram, S., Vasudevan, U., Pradeep, K., Nepolian, M., Prasanna, M. V, Adithya, V. S., Thilagavathi, R., Thivya, C., & Panda, B. (2020). *Determination of the major geochemical processes of groundwater along the Cretaceous-Tertiary boundary of Trichinopoly , Tamilnadu , India*.

Devic, G., Djordjevic, D., & Sakan, S. (2014). Natural and anthropogenic factors affecting the groundwater quality in Serbia. *Science of the Total Environment*, *468*, 933–942.

Díaz-Puga, M. A., Vallejos, A., Sola, F., Daniele, L., Molina, L., & Pulido-Bosch, A. (2016). Groundwater flow and residence time in a karst aquifer using ion and isotope characterization. *International Journal of Environmental Science and Technology*, *13*, 2579–2596.

Dula, W. D. (2010). *GIS and Remote Sensing Based Land Suitability Analysis for Agricultural Crops in Mojo Watershed, Upper Awash Sub Basin, Ethiopia*. Addis Ababa University.

Egbueri, J. C., Mgbenu, C. N., & Chukwu, C. N. (2019). Investigating the hydrogeochemical processes and quality of water resources in Ojoto and environs using integrated classical methods. *Modeling Earth Systems and Environment*, *5*(4), 1443–1461.

Elango, L., & Kannan, R. (2007). Rock–water interaction and its control on chemical composition of groundwater. *Developments in Environmental Science*, *5*, 229–243.

Eshetu, M. (2021). Hydro-climatic Variability and Trend Analysis of Modjo River Watershed, Awash River Basin of Ethiopia. *Journal of Environment and Earth Science*, *11*(Figure 1), 1–8. https://doi.org/10.7176/jees/11-9-04

Fikirie, K., Bezu, A., Eshetu, M., Bekele, D., & Rabo, M. (2020). Evaluate Technical Standards of Implemented Soil Bund in Central Rift Valley of Ethiopia: The Case of Adama, Lume and Dodota Districts. *Agriculture and Food Sciences Research*, *7*(1), 51–57. https://doi.org/10.20448/journal.512.2020.71.51.57

Furi, W., Razack, M., Abiye, T. A., Ayenew, T., & Legesse, D. (2011). Fluoride enrichment mechanism and geospatial distribution in the volcanic aquifers of the Middle Awash basin, Northern Main Ethiopian Rift. *Journal of African Earth Sciences*, *60*(5), 315–327. https://doi.org/10.1016/j.jafrearsci.2011.03.004

Gaillardet, J., Dupre, B., Louvat, P., & Allegre, C. J. (1999). <van Rie et al. (1999).pdf>. *Chemical Geology*, *159*(8), 3–30.

Ganyaglo, S. Y., Banoeng-Yakubo, B., Osae, S., Dampare, S. B., & Fianko, J. R. (2011). Water quality assessment of groundwater in some rock types in parts of the eastern region of Ghana. *Environmental Earth Sciences*, *62*, 1055–1069.

Gastmans, D., Hutcheon, I., Menegário, A. A., & Chang, H. K. (2016). Geochemical evolution of groundwater in a basaltic aquifer based on chemical and stable isotopic data: Case study from the Northeastern portion of Serra Geral Aquifer, São Paulo state (Brazil). *Journal of Hydrology*, *535*, 598–611.

Gebere, A., Kawo, N. S., Karuppannan, S., Hordofa, A. T., & Paron, P. (2021). Numerical modeling of groundwater flow system in the Modjo River catchment, Central Ethiopia. *Modeling Earth Systems and Environment*, *7*(4), 2501–2515.

Giménez-Forcada, E., Bencini, A., & Pranzini, G. (2010). Hydrogeochemical considerations about the origin of groundwater salinization in some coastal plains of Elba Island (Tuscany, Italy). *Environmental Geochemistry and Health*, *32*, 243–257.

Gleeson, T., Cuthbert, M., Ferguson, G., & Perrone, D. (2020). Global groundwater sustainability, resources, and systems in the Anthropocene. *Annual Review of Earth and Planetary Sciences*, *48*(1), 431–463.

Hadnott, B. A., Ehlmann, B. L., & Jolliff, B. L. (2017). Mineralogy and chemistry of San Carlos high-alkali basalts: analyses of alteration with application for Mars exploration. *American Mineralogist*, *102*(2), 284–301.

Haji, M., Qin, D., Guo, Y., Li, L., Wang, D., Karuppannan, S., & Shube, H. (2021). Origin and geochemical evolution of groundwater in the Abaya Chamo basin of the Main Ethiopian Rift: application of multi-tracer approaches. *Hydrogeology Journal*, *29*(3), 1219–1238. https://doi.org/10.1007/s10040-020-02291-y

Herman, J. S., & Gellasch, C. A. (2021). *Geohydrology: Hydrogeochemistry*.

Hinman, N. W., & Hinman, N. W. (2013). *ScholarWorks at University of Montana Water-rock interaction and life Let us know how access to this document benefits you . Water-rock interaction and life*. 354–359. https://doi.org/10.1016/j.proeps.2013.03.228

Hiscock, K. M. (2011). Groundwater in the 21st century–meeting the challenges. *Sustaining Groundwater Resources: A Critical Element in the Global Water Crisis*, 207–225.

Hiscock, K. M., Rivett, M. O., & Davison, R. M. (2002). Sustainable groundwater development. *Geological Society, London, Special Publications*, *193*(1), 1–14.

Hsieh, W. W. (2001). Nonlinear principal component analysis by neural networks. *Tellus A*, *53*(5), 599–615.

Huang, T., & Ma, B. (2019). The origin of major ions of groundwater in a loess aquifer. *Water*, *11*(12), 2464.

Ibrahim, R. G. M., Korany, E. A., Tempel, R. N., & Gomaa, M. A. (2019). Processes of water–rock interactions and their impacts upon the groundwater composition in Assiut area, Egypt: applications of hydrogeochemical and multivariate analysis. *Journal of African Earth Sciences*, *149*, 72–83.

Kawo, N. S., & Karuppannan, S. (2018a). Groundwater quality assessment using water quality index and GIS technique in Modjo River Basin, central Ethiopia. *Journal of African Earth Sciences*, *147*, 300–311.

Kawo, N. S., & Karuppannan, S. (2018b). Groundwater Quality Assessment Using Water Quality Index and GIS Technique in Modjo River Basin, Central Ethiopia. *Journal of African Earth Sciences*. https://doi.org/10.1016/j.jafrearsci.2018.06.034

Kazmin, V., & Seifemichael, B. (1978). Geology and development of the Nazareth area, Northern Ethiopia Rift. *Geol. Surv. of Ethiopia*.

Kebede, S. (2012). *Groundwater in Ethiopia: features, numbers and opportunities*. Springer Science & Business Media.

Kebede, S., Travi, Y., Asrat, A., Alemayehu, T., Ayenew, T., & Tessema, Z. (2008). Groundwater origin and flow along selected transects in Ethiopian rift volcanic aquifers. *Hydrogeology Journal*, *16*, 55–73.

Keranen, K., & Klemperer, S. L. (2008). Discontinuous and diachronous evolution of the Main Ethiopian Rift: Implications for development of continental rifts. *Earth and Planetary Science Letters*, *265*(1–2), 96–111.

Lakshmanan, E., Kannan, R., & Kumar, M. S. (2003). Major ion chemistry and identification of hydrogeochemical processes of ground water in a part of Kancheepuram district, Tamil Nadu, India. *Environmental Geosciences*, *10*(4), 157–166.

Long, D. T., Voice, T. C., Niagolova, N. D., & McElmurry, S. P. (2012). Effects of human activities on karst groundwater geochemistry in a rural area in the Balkans. *Applied Geochemistry*, *27*(10), 1920–1931.

Lowenstern, J. B. (2001). Carbon dioxide in magmas and implications for hydrothermal systems. *Mineralium Deposita*, *36*, 490–502.

Malago, J. (2017). Fluoride Levels in Surface and Groundwater in Africa: A Review. *American Journal of Water Science and Engineering*, *3*(1), 1. https://doi.org/10.11648/j.ajwse.20170301.11

Mamo, S. (2002). Water balance evaluation, leakage rate and total water loss of Koka Reservoir, Ethiopia: comments on previous studies and new determinations. *SINET: Ethiopian Journal of Science*, *25*(1), 141–150.

Mas-Pla, J., & Menció, A. (2019). Groundwater nitrate pollution and climate change: learnings from a water balance-based analysis of several aquifers in a western Mediterranean region (Catalonia). *Environmental Science and Pollution Research*, *26*(3), 2184–2202.

Mechal, A., Birk, S., Dietzel, M., Leis, A., & Birk, S. (2017). *Groundwater flow dynamics in the complex aquifer system of Gidabo River Basin (Ethiopian Rift): a multi-proxy approach*. 519–538. https://doi.org/10.1007/s10040-016-1489-5

Mengistu, H. A., Demlie, M. B., & Abiye, T. A. (2019). *Groundwater resource potential and status of groundwater resource development in Ethiopia*.

Mohamed, A., Asmoay, A., Alshehri, F., Abdelrady, A., & Othman, A. (2022). Hydro-geochemical applications and multivariate analysis to assess the water–rock interaction in arid environments. *Applied Sciences*, *12*(13), 6340.

Mohamed, M. M., & Elmahdy, S. I. (2015). Natural and anthropogenic factors affecting groundwater quality in the eastern region of the United Arab Emirates. *Arabian Journal of Geosciences*, *8*, 7409–7423.

Mohr, P. A. (1971). Ethiopian rift and plateaus: some volcanic petrochemical differences. *Journal of Geophysical Research*, *76*(8), 1967–1984.

Mohr, P., & Gouin, P. (1976). Ethiopian Rift System. *Geodynamics: Progress and Prospects*, *5*, 81–87.

Möller, P., Rosenthal, E., Inbar, N., & Magri, F. (2016). Hydrochemical considerations for identifying water from basaltic aquifers: The Israeli experience. *Journal of Hydrology: Regional Studies*, *5*, 33–47.

Mondal, N. C., Singh, V. P., Singh, V. S., & Saxena, V. K. (2010). Determining the interaction between groundwater and saline water through groundwater major ions chemistry. *Journal of Hydrology*, *388*(1–2), 100–111.

Morán-Ramírez, J., Ledesma-Ruiz, R., Mahlknecht, J., & Ramos-Leal, J. A. (2016). Rock–water interactions and pollution processes in the volcanic aquifer system of Guadalajara, Mexico, using inverse geochemical modeling. *Applied Geochemistry*, *68*, 79–94.

Morbidelli, L., & Piccirillo, E. M. (1973). Tectonics and volcanism in the Main Ethiopian Rift (Preliminary report). *Bollettino Della Societa Geologica Italiana*, *92*(2), 273–286.

Naik, P., Naik, G., & Patil, M. (2022). Conceptualizing Python in Google COLAB. *India: Shashwat Publication*.

Negash, T. W., Abagale, F. K., & Baatuuwie, B. N. (2022). Impact of land-use and land-cover change on watershed hydrology: a case study of Mojo watershed, Ethiopia. *Environmental Earth Sciences*, *81*(23), 536.

Olumana, M., & Loiskandl, W. (2015). Journal of Hydrology : Regional Studies Hydrochemical characterization of various surface water and groundwater resources available in Matahara areas , Fantalle Woreda of Oromiya region. *Journal of Hydrology: Regional Studies*, *3*, 444–456. https://doi.org/10.1016/j.ejrh.2015.02.007

Piper, A. M. (1944). A graphic procedure in the geochemical interpretation of water-analyses. *Eos, Transactions American Geophysical Union*, *25*(6), 914–928.

Sabarathinam, A. P., & Ramachandran, M. (2011). Use of hydrochemistry and stable isotopes as tools for groundwater evolution and contamination investigations. *Geosciences*, *1*(1), 16–25.

Sadeghi, A., Galalizadeh, S., Zehtabian, G., & Khosravi, H. (2021). Assessing the change of groundwater quality compared with land-use change and precipitation rate (Zrebar Lake's Basin). *Applied Water Science*, *11*, 1–15.

Sallis, J. F., Conway, T. L., Prochaska, J. J., McKenzie, T. L., Marshall, S. J., & Brown, M. (2001). The association of school environments with youth physical activity. *American Journal of Public Health*, *91*(4), 618.

Şen, Z. (2014). *Practical and applied hydrogeology*. Elsevier.

Sharma, M. K., & Kumar, M. (2020). Sulphate contamination in groundwater and its remediation: an overview. *Environmental Monitoring and Assessment*, *192*, 1–10.

Sisay, B. M., Nedaw, D., Birhanu, B., & Gigar, A. G. (2023). Application of SWAT and MODFLOW models for characterization of surface–groundwater interaction in the Modjo River catchment, central Ethiopia. *Environmental Earth Sciences*, *82*(13), 341.

Tekile, A. K. (2023). Suitability assessment of surface water quality for irrigation: A case study of Modjo River, Ethiopia. *Journal of Environmental and Public Health*, *2023*(1), 1482229.

Tweed, S. O., Weaver, T. R., Cartwright, I., & Schaefer, B. (2006). Behavior of rare earth elements in groundwater during flow and mixing in fractured rock aquifers: an example from the Dandenong Ranges, southeast Australia. *Chemical Geology*, *234*(3–4), 291–307.

Varol, S., & Davraz, A. (2014). Assessment of geochemistry and hydrogeochemical processes in groundwater of the Tefenni plain (Burdur/Turkey). *Environmental Earth Sciences*, *71*, 4657–4673.

Vaux, H. (2011). Groundwater under stress: the importance of management. *Environmental Earth Sciences*, *62*, 19–23.

Wang, Y., Zheng, C., & Ma, R. (2018). Safe and sustainable groundwater supply in China. *Hydrogeology Journal*, *5*, 1301–1324.

WHO. (2018). A global overview of national regulations and standards for drinking-water quality. In *Water, Sanitation, Hygiene and Health (WSH)*. https://www.who.int/publications/i/item/9789241513760

Wondimu Negash, T. (2021). *Impact of landuse and landcover change on watershed hydrology: a case study of mojo watershed, Ethiopia*. University for Development Studies.

Zhang, Y. Q., Wang, G. W., Wang, S. Q., Yuan, R. Q., Tang, C. Y., & Song, X. F. (2018). Hydrochemical characteristics and geochemistry evolution of groundwater in the plain area of the Lake Baiyangdian watershed, North China Plain. *Journal of Groundwater Science and Engineering*, *6*(3), 220–233. https://doi.org/10.19637/j.cnki.2305-7068.2018.03.007

APPENDIX

Appendix 1: Rainfall data of the study area

Stations	Jan	Feb	Mar	April	May	June	July	Aug	Sep	Oct	Nov	Dec
Bishoftu	10.8	14.4	49.7	54.4	42.7	107	222.6	211.5	97.3	23.8	7.6	6.6
Mojo	14.2	16.1	53.1	59.9	65.8	114	300	239.2	114.5	37.9	10	4.5
Ejere	15.2	18.1	45.2	53.3	54.1	87.5	250	270.6	110.7	32.5	16.6	10.5
Koka	12.9	16	45.3	40.5	55	86.6	243	224	94	33.8	12	9.4
Chafe D	14.6	20.8	35.4	56.7	57.6	99.7	236.5	246.7	98	22.6	7.8	5.3

Appendix 2: Average Monthly Maximum and Minimum Temperature

	Jan	Feb	Mar	April	May	June	July	Aug	Sep	Oct	Nov	Dec
Bis,Max	26.68	28.32	28.64	28.67	29.23	27.61	24.49	24.11	25.42	26.37	25.9	25.9
Bis.min	9.09	10.43	12.35	13.51	13.12	13.08	13.60	13.64	12.46	10.04	8.82	8.49
Moj Max	29.44	30.32	31.17	31.11	31.15	30.12	26.58	26.29	27.91	29.12	29	28.6
Moj min	8.93	10.40	12.38	13.27	13.39	12.91	13.04	13.08	12.44	10.76	9.57	7.93
Chaf max	22.96	24.40	25.06	25.08	25.49	24.53	21.62	21.57	22.56	22.50	22	21.9
Chaf min	8.91	10.31	11.72	12.44	11.82	11.42	11.56	11.51	11.25	10.31	8.90	7.95
Ejere Max	24.64	25.05	25.56	25.58	26.15	25.47	22.56	22.00	22.85	23.75	24.5	24.3
Ejere Min	10.57	11.13	11.54	12.23	12.95	11.91	11.52	11.27	11.39	11.11	10.7	9.85
Koka Max	30.00	30.52	32.48	32.90	32.92	31.96	29.38	29.21	30.14	29.60	29.4	28.7
Koka Min	12.35	13.88	15.08	15.56	15.74	15.23	14.59	14.36	14.60	12.95	12.2	11.3

Appendix 3: General ionic parameters of the study area (UM-upper Modjo, MM-medium Modjo, LM-lower Modjo)

											meq/L							
No.	Site Name	Well ID	UTME	UTMN	Adindan Z	Elev, m	EC (µS/cm)	Ph	TDS	Na	K	Ca	Mg	F	Cl	NO3	HCO3	SO4
UM-5	Aroje		517106	989113	37	2249	488	7.86	268	2.284	0.107	1.832	1.571	-0.047	-0.113	-0.011	-5.359	-0.004
UM-7	Cheleleke		522057	991458	37	2328	463	7.97	255	1.261	0.243	3.827	0.239	-0.037	-0.158	-0.019	-4.759	-0.002
UM-8	Woberi		524014	1000880	37	2453	391	7.13	196	0.683	0.332	2.822	0.319	-0.042	-0.367	-0.011	-3.799	-0.109
UM-9	Gorgoru		514481	986473	37	2209	602	7.92	360	2.097	0.092	2.036	1.619	-0.042	-0.494	0.000	-4.678	-0.236
UM-11	Uso Cheleleka		522015	990828	37	2287	507	7.83	276	0.652	0.125	3.583	1.128	-0.018	-0.087	0.000	-4.319	-0.331
UM-12	Bui Gundo		501010	986980	37	2389	513	6.79	326	0.495	0.159	3.054	2.457	-0.021	-0.082	0.000	-5.358	-0.143
UM-13	Kike		506095	985394	37	2233	610	6.73	354	0.991	0.097	3.095	1.933	-0.025	-0.113	0.000	-6.398	-0.152
UM-16	Oda		506825	996633	37	2454	317	7.5	202	0.820	0.294	2.674	0.447	-0.025	-0.234	0.000	-3.559	-0.135
UM-21	Cheleleka		520222	992244	37	2313	563	7.27	372	1.320	0.243	3.992	0.987	-0.063	-0.124	0.000	-5.998	-0.450
UM-23	Wutafo		527758	999086	37	2427	427	7.52	268	0.779	0.205	2.874	1.066	-0.034	-0.508	0.000	-4.321	-0.162
MM-1	Hidi	APW-003-	506138	970846	37	1886	651	7.38	392	4.437	0.105	1.176	0.638	-0.034	-0.975	-0.010	-5.038	-0.664
MM-2	Denkaka	APW-005-	507556	958248	37	1855	670	7.61	404	2.653	0.327	2.515	2.093	-0.036	-0.490	-0.115	-6.238	-0.066
MM-3	Adaa	APW-006-	504300	960685	37	1872	659	7.04	420	2.392	0.294	2.810	2.519	-0.033	-0.462	-0.109	-6.558	-0.168
MM-4	Adaa	APW-007-	503475	960957	37	1879	666	8.52	434	2.697	0.294	1.996	2.764	-0.043	-0.427	-0.102	-5.470	-0.927
MM-5	Bali-Abo	APW-008-	511723	958922	37	1841	693	6.63	452	2.827	0.486	3.563	0.207	-0.027	-0.347	-0.043	-6.958	-0.067
MM-6	Kaliti	APW-009-	503717	971356	37	1897	487	7	320	3.306	0.315	1.176	0.712	-0.041	-0.334	-0.005	-4.638	-0.004
MM-7	Byo-Bske	APW-010-	509308	957888	37	1801	690	6.66	404	3.393	0.095	2.555	1.501	-0.033	-0.411	-0.074	-6.398	-0.313
MM-8	Beuo Bese	APW-012-	511430	957367	37	1816	667	6.81	440	2.566	0.486	2.655	1.463	-0.034	-0.427	-0.032	-6.900	-0.293
MM-9	Hidi	APW-014-	508991	969895	37	1917	700	7.1	476	1.957	0.396	3.772	1.670	-0.042	-0.539	-1.379	-5.762	-0.639
MM-10	Denkaka	APW-017-	505863	960482	37	1877	637	6.87	398	2.566	0.151	3.353	1.422	-0.039	-0.411	-0.078	-6.558	-0.171
MM-11	Denkaka	APW-020-	508432	959037	37	1850	671	7.36	398	2.479	0.325	2.465	2.063	-0.031	-0.411	-0.257	-6.344	-0.176
MM-12	Adaa	APW-021-	506615	961264	37	1841	662	7.26	390	2.436	0.302	2.675	2.053	-0.037	-0.359	-0.179	-6.638	-0.296
MM-13	Algae	APW-022-	508471	961147	37	1851	716	7.35	412	4.002	0.271	2.435	1.382	-0.041	-0.561	-0.040	-6.718	-0.236
MM-14	Algae	APW-023-	507557	961072	37	1855	574	7.45	370	3.045	0.263	2.191	1.122	-0.037	-0.462	-0.059	-6.318	-0.308
MM-15	Girime Esi	APW-024-	511510	958955	37	1842	676	7.33	426	3.001	0.230	3.624	0.765	-0.036	-0.449	-0.027	-6.598	-0.375
MM-16	Katila	APW-028-	506220	968104	37	1880	1554	6.71	1060	12.005	0.882	3.110	1.501	-0.051	-0.975	-0.010	-16.395	-1.895
MM-17	Katila	APW-039-	507157	977107	37	1877	1528	6.78	1030	9.047	0.831	8.723	0.409	-0.043	-0.801	-0.161	-16.395	-1.637
MM-18	Katila	APW-040-	508515	967494	37	1848	1145	7.22	740	6.351	0.754	3.433	2.369	-0.036	-0.693	-0.023	-10.077	-1.555
MM-19	Katila	APW-041-	509241	967123	37	1841	910	6.63	590	3.306	0.435	4.737	1.949	-0.028	-0.564	-0.465	-8.397	-1.094
MM-20	Denkaka	APW-046-	505273	966105	37	1882	994	7.09	610	5.655	0.754	2.124	1.650	-0.042	-1.001	-0.064	-9.307	-0.735
MM-21	Serdo	APW-058-	507153	965139	37	1844	671	6.71	673	2.919	0.172	0.335	0.552	-0.035	-0.190	-0.108	-0.110	-0.140
MM-22	Adaa	APW-060-	509189	965087	37	1856	909	6.73	592	4.437	0.806	3.034	1.351	-0.052	-0.427	-0.036	-8.677	-0.583
MM-23	Goro	APW-063-	502085	964206	37	1873	841	7.57	504	4.002	0.079	2.541	1.988	-0.041	-0.975	-0.130	-7.598	-0.435
MM-24	Denkaka	APW-064-	504379	964125	37	1880	723	7.22	496	4.263	0.422	1.858	2.289	-0.038	-0.590	-0.147	-8.637	-0.312
MM-25	Denkaka	APW-066-	506154	964148	37	1820	743	6.87	478	4.002	0.281	2.541	1.238	-0.028	-0.534	-0.028	-6.322	-0.470
MM-26	Katila	APW-068-	508223	964173	37	1841	946	6.63	620	4.219	0.844	3.337	1.238	-0.048	-0.507	-0.037	-9.197	-0.717
MM-27	Ada'a	APW-069-	504784	959857	37	1863	562	7.72	380	1.435	0.128	3.433	1.343	-0.037	-0.381	-0.415	-5.398	-0.650
MM-28	Denkaka	APW-071-	508697	959616	37	1850	676	7.2	440	3.132	0.358	2.725	2.032	-0.036	-0.417	-0.174	-6.558	-0.345
MM-29	Denkaka	APW-072-	507630	959592	37	1882	660	7.46	392	2.523	0.307	0.599	1.382	-0.040	-0.411	-0.154	-6.638	-0.212
MM-30	Denkaka	APW-073-	502454	962792	37	1884	633	6.95	370	2.131	0.274	2.844	1.538	-0.036	-0.411	-0.261	-6.298	-0.230
MM-31	Denkaka	APW-074-	504203	963155	37	1875	628	7.06	378	2.218	0.289	2.435	2.132	-0.034	-0.359	-0.143	-6.038	-0.176
MM-32	Denkaka	APW-075-	505095	962950	37	1863	651	6.96	374	2.110	0.261	2.994	1.619	-0.034	-0.436	-0.199	-5.920	-0.350
MM-33	Denkaka	APW-076-	506213	963103	37	1886	963	6.75	628	6.090	0.921	3.473	1.106	-0.042	-0.565	-0.066	-9.687	-0.795
MM-34	Denkaka	APW-079-	504753	958477	37	1874	696	7.31	428	2.697	0.330	3.034	2.026	-0.045	-0.462	-0.102	-6.918	-0.379
MM-35	Denkaka	APW-080-	505855	958505	37	1874	694	7.18	436	2.131	0.284	4.391	0.987	-0.043	-0.427	-0.139	-7.438	-0.407
MM-36	Denkaka	APW-082-	503185	962173	37	1884	696	7.22	486	3.045	0.307	3.074	1.580	-0.004	-0.561	-0.205	-6.927	-0.081
MM-37	Denkaka	APW-084-	505077	962102	37	1872	638	6.8	440	2.914	0.284	2.635	1.461	-0.032	-0.590	-0.392	-6.588	-0.291
MM-38	Denkaka	APW-085-	506109	962140	37	1880	733	6.82	484	3.741	0.550	2.427	1.200	-0.032	-0.411	-0.061	-7.647	-0.359
MM-39	Algae	APW-086-	507472	962097	37	1850	716	7.35	412	4.002	0.271	2.435	1.382	-0.041	-0.561	-0.040	-6.718	-0.236
MM-40	Denkaka	APW-088-	503018	959480	37	1880	706	7.38	432	2.610	0.320	3.034	1.838	-0.039	-0.539	-0.063	-6.994	-0.139
MM-41	Denkaka	APW-089-	506490	957774	37	1861	721	7.24	454	2.262	0.384	3.194	2.014	-0.033	-0.641	-0.100	-6.458	0.000
MM-42	A/Jegola	APW-090-	511524	956435	37	1824	689	7.03	440	2.697	0.473	2.541	2.364	-0.029	-0.411	-0.101	-7.598	-0.287
MM-58	Denkaka	APW-094-	510602	956528	37	1841	704	7.16	402	2.827	0.092	2.806	1.876	-0.038	-0.461	-0.074	-6.798	-0.290
MM-43	Beyo-bese	APW-100-	510664	957391	37	1841	676	7.1	390	2.653	0.473	2.395	1.817	-0.041	-0.334	-0.052	-6.398	-0.464
MM-44	Ude	AMW21	506765	957179	37	1836	682	7.4	468	2.523	0.358	4.780	0.294	-0.068	-0.587	-0.121	-6.678	-1.203
MM-45	Borora	AMW22B	504878	970766	37	1879	549	7.3	380	2.131	0.358	2.735	1.053	-0.053	-0.336	-0.090	-5.794	-0.164
MM-46	Shimbira I	AdBh0063	500766	973335	37	1905	615	8	220	1.244	0.228	2.859	1.538	-0.021	-0.299	-0.019	-5.598	0.000
MM-47	Shimbira I	AdBh0064	500494	974376	37	1914	530	7.09	350	1.348	0.174	3.907	0.979	-0.004	-0.164	-0.218	-5.710	-0.044
MM-48	Shimbira r	AdBh0065	500424	974376	37	1914	615	8.3	397	1.435	0.230	2.395	1.259	-0.026	-0.499	-0.031	-4.199	0.000
MM-49	Air force	AdBh0070	500909	964676	37	1903	628	7.48	391	2.175	0.256	3.553	1.242	-0.024	-0.434	-0.282	-6.214	-0.286
MM-50	Biyo Bese	AdBh0085	507714	955875	37	1855	728	7.44	476	2.871	0.307	3.688	1.999	-0.024	-0.434	-0.161	-7.558	-0.154
MM-51	Health Co	AdBh0261	497100	968198	37	1901	453	7.49	306	1.827	0.307	1.607	1.176	-0.017	-0.271	-0.161	-4.446	-0.063
MM-53	Genesis F	AdBh0949	495447	968068	37	1902	469	7.57	286	1.000	0.159	0.000	1.974	-0.030	-0.226	0.000	-5.015	-0.171
MM-54	Elfora Agr	AdBh0987	494145	966864	37	1930	480	7.38	196	0.961	0.095	2.495	1.876	-0.037	-0.056	-0.108	0.000	-0.148
MM-55	Airforce N	AdBh1006	499500	964500	37	1890	576	7.8	194	2.810	0.307	2.241	2.402	-0.042	-0.801	-0.144	-6.598	-0.090
MM-56	Blue 0e Pl	AdBh1024	495765	966397	37	1910	614	7.69	375	1.479	0.230	2.196	2.962	-0.033	-0.197	-0.081	0.000	-0.146
MM-57	Veternary	AdBh1027	500078	968505	37	1880	1041	7.87	635	6.003	0.307	1.796	2.962	-0.038	-0.073	-0.007	-10.243	-0.125
LM-1	Mudasenk	APW-011-	506187	943199	37	1884	685	7.85	480	6.090	0.281	1.006	0.189	-0.069	-0.347	-0.159	-5.358	-2.376
LM-3	A/Jegola	APW-092-	513546	953365	37	1801	475	7.05	306	1.914	0.320	2.010	0.863	-0.044	-0.214	-0.019	-4.798	-0.137
LM-4	Lume	APW-095-	509971	959175	37	1850	713	7.1	460	3.175	0.460	2.617	1.538	-0.023	-0.561	-0.071	-6.958	-0.232
LM-5	Gafat#1	AdBh0072	507491	952694	37	1862	950	7.7	386	2.514	0.256	3.278	1.464	-0.079	-0.801	-0.044	-6.798	0.000
LM-6	Gafat#7	AdBh0078	509385	950325	37	1994	915	7.9	340	3.254	0.435	2.600	1.802	-0.047	-0.750	-0.026	-6.998	-0.291
LM-7	Gafat#8	AdBh0079	509020	950736	37	1795	915	8	350	3.106	0.358	2.959	1.522	-0.058	-0.587	-0.040	-7.598	0.000
LM-8	Gafat#9	AdBh0080	508684	951058	37	1806	915	7.6	395	2.662	0.332	3.698	1.497	-0.047	-1.001	-0.148	-6.998	0.000
LM-9	Gafat#10	AdBh0081	507950	951364	37	1819	741	7.15	482	3.045	0.460	3.643	1.645	-0.100	-0.513	-0.169	-7.683	-0.187
LM-10	Lume#3	AdBh0087	512957	947774	37	1783	519	7.35	376	2.262	0.332	2.620	0.930	-0.074	-0.164	-0.169	-5.459	-0.082
LM-12	Modjo#2	AdBh0091	511976	948671	37	1786	618	7.8	750	3.328	0.384	2.445	0.938	-0.047	-0.350	-0.040	-6.703	0.000
LM-13	Modjo#3	AdBh0092	512408	948682	37	1782	590	7.25	390	2.827	0.307	3.019	0.757	-0.058	-0.164	-0.053	-6.255	-0.022
LM-14	Modjo#1	AdBh0093	512011	949196	37	1785	673	8.3	449	3.032	0.332	2.345	0.905	-0.043	-0.401	-0.014	-5.598	0.000