Investigation of Water Quality and Evaluation of its suitability for Irrigation and Drinking purposes, Zamra Catchment, Northern Ethiopia

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July, 2020

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ABSTRACT

The study is conducted in Zamra catchment, Tigray, northern Ethiopia. The study is focused on the investigation of water-related problems and the geochemical process that controls the geochemistry of groundwater. The analyzed result from primary water samples is in Aquachem and NETPATH simple geochemical model for the geochemical analysis and presentation of the water quality data.

The finding results show that the dominant major ions are HCO3> SO4> Ca > Na >Mg >K, respectively. The study area is dominated by magnesium bicarbonate water type specifically Na-Mg-Ca-HCO3, Ca-HCO3-SO4 followed by chloride water types. The chloride water type is observed only in SHW19. The geochemical processes that control the chemical composition of groundwater are silicate weathering, precipitation of calcite, and dissolution of dolomite and anthropogenic activities. There are also impact of the anthropogenic activity that deteriorates water quality.

Suitability of water for irrigation and drinking purpose is evaluated using the standards stated by FAO, WHO, and Ethiopian standards. 70 % of groundwater samples have high to very high salinity hazard.

Most of the water samples collected are not desirable for drinking purposes. Na is found within the permissible limit except in SHW19.

Key Words: Water Quality, Geochemical process, NETPATH model, Irrigation, Zamra catchment

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LISTS OF ABBREVIATIONS

Acronyms	Description
DW	Deep Well
ESA	European Space Agency
EENSAT	Ethiopian Educational Network to Support Agricultural Transformation
FAO	Food and Agricultural Organization
GPS	Geographic Positioning System
HDW	Hand Dug Well
HCl	Hydrochloric Acid
ICP-OES	Inductively Coupled plasma Optical Emission Spectrometry
LULC	Land Use Land Cover
MAR	Magnesium Adsorption Ratio
KR	Kelly's Ratio
HNO_3^-	Nitric Acid
% Na	Percent Sodium
PI	Permeability Index
PH	Power of Hydrogen
SHW	Shallow Well
SAR	Sodium Adsorption Ratio
TWRB	Tigray Water Resource Bureau
WREM	Water Resource and Environmental Management
WQ	Water Quality
SI	Saturation Index
Mg/l	Milligram per liter
Meq/l	Milliequivalent per liter

LISTS OF SYMBOLES

Agronomy	Description	Unit
Al	Aluminium	mg/l
As	Arsenic	mg/l
B	Boron	mg/l
Ba	Barium	mg/l
Be	Beryllium	mg/l
Ca	Calcium	mg/l
Cr	Chromium	mg/l
Co	Cobalt	mg/l
Cu	Copper	mg/l
CO_3	Carbonate	mg/l
Cl	Chloride	mg/l
EC	Electrical Conductivity	µs/cm
Fe	Iron	mg/l
HCO_3	Bicarbonate	mg/l
K	Potassium	mg/l
Li	Lithium	mg/l
Mg	Magnesium	mg/l
Mn	Manganese	mg/l
Na	Sodium ion	mg/l
Pb	Lead	mg/l
TDS	Total Dissolved Solids	mg/l
TH	Total Hardness	mg/l
Se	Selenium	mg/l
Zn	Zinc	mg/l

1 INTRODUCTION

1.1 Background and Justification

"Water is the most common and important substance within the earth and plays a central role in any of sectoral activities such as irrigation, industry purpose, and human consumption" (Brhane, 2018, p. 214) and it is indispensable for both, the existence of life, economic development and food security (Choudhary, Dhakad, & Jain, 2014; Mandal, Dutta, Pramanik, & Kole, 2019).

In developing countries, particularly in sub-Saharan African countries like Ethiopia, more attention is given to water resource assessment than management and protection. The issue of water quality, the demand of freshwater for human consumption and agriculture is more critical in recent years due to the rapid growth of urbanization and industrialization, rapid growth of population, and intense agricultural extensions (Aghazadeh, Chitsazan, & Golestan, 2017; Brhane, 2018; Choudhary et al., 2014; Kahsay, Gebreyohannes, Tesema, & Emabye, 2019; Mandal et al., 2019; Mengistu, Demlie, & Abiye, 2019).

As stated by Ismail & El-Rawy (2018), further development and planning is required in arid and semiarid regions, especially in areas were suffering from poor water quality and water budget deficit due to the shortage of precipitation and high evaporation rates which leads to a critical problem for water resource management.

Water with good quality is essential beyond its availability, and it is important to support life in a good manner. Surface and Groundwater resources are not pure in their chemical composition. It contains dissolved minerals, inorganic constituents, salts, cations, and anions with variable concentration and composition that causes pollution and affects the usefulness of water for agriculture, industry and household use. Determining of the chemical, physical, and microbiological properties of water have an important role in assessing and evaluating its quality criteria for a particular usage (Aghazadeh et al., 2017; Kahsay et al., 2019; Sheikhy Narany et al., 2014; Yang, Li, Ma, Wang, & Martín, 2016).

There are several studies conducted on water quality issues and the identification of the hydrogeochemical process. The main factors are high evaporation rate and limited discharge, excessive pumping of groundwater and seawater-fresh water mixing. These results increase the salt concentration of groundwater. Identifying the water quality problems and determining the hydrogeochemical process is a crucial issue for water resource management (Aghazadeh et al., 2017; Numanbakth, Howladar, Faruque, Sohail, & Rahman, 2019; Sheikhy Narany et al., 2014).

Testing of water for its physicochemical property is a first and essential step to evaluate its suitability for agricultural usage, industrial purpose, or household use and to prepare a treatment plan to protect water from pollution and to reduce water quality induced problems (Dinka, 2016).

Use of water with high salinity, toxicity, or sodicity for irrigation purposes destroys soil structure, damage the irrigation equipment. It results in reducing crop productivity and production, or it can cause total crop failure. And it results in health problems if it is used for human consumption (Dinka, 2016; Rizani, Laze, & Ibraliu, 2017). Water quality problem does not only mean excess constituents, but it also has effects on human health and agriculture if there is a deficiency of mineral constituents and ions in the water (Kahsay et al., 2019; Reimann et al., 2003).

1.2 Research problem

Ethiopia has high spatial and temporal variability in hydrogeology. It is characterized by a very complex geological evolutionary process, and climatic variability. For this reason, the quality of water is variable spatially and temporally depending on geology, land use land cover and climate. There is no complete information on water quality in the country particularly from Zamra catchment, selected study area, no recent water quality investigation has been conducted. In sub-Saharan African countries particularly in Ethiopia, there is a lack of water resource management and protection (Girmay et al., 2015; Mengistu et al., 2019).

There are several pieces of research carried out on the assessment and evaluation of water quality for irrigation and drinking purpose in the world as well as in the country and the region. But there is no equal water quality criteria or composition over the world to use the water directly for either agriculture, industry or human consumption because it is highly dependent on the local conditions such as geology and LULC. Water quality should be always assessed, both spatially and temporally (Dinka, 2016; Kahsay et al., 2019; Namugize, Jewitt, & Graham, 2018; Rizani et al., 2017; Tadesse, Bheemalingeswara, & Berhane, 2009).

According to National Nile Basin Water Quality Monitoring Baseline Report and other researches conducted, there are water quality data's collected and analyzed from Tekeze basin, but this is only for some chemical property of groundwater and does not include the physical property of surface water of Zamra catchment, and most of the studies are related to groundwater potential rather than water quality (Girmay et al., 2015). The water quality information on the physicochemical parameters is limited in the northern part relative to the southern part of Ethiopia (Wondim, 2016)

In the study area, Zamra catchment, agriculture is the most common activity, and it is the main source of economy for the local people as well as for the country. The community uses both surface and groundwater for irrigation and drinking purpose, but its quality has not been yet determined whether it fits or not for this usage. Both surface and groundwater used for irrigation purposes are not yet been checked for its quality and suitability and the spatial distribution of water quality of Zamra catchment has not yet been studied (Girmay, 2015; Merid, n.d.). In this research work, the water quality will be assessed and evaluated by comparing its constituents with national standards and international guidelines for irrigation purposes and human consumption. The spatial distribution of the water quality criteria in relation to geology and land use land cover will also be addressed.

This research work is supported by the Ethiopian Education Network to Support Agricultural Transformation (EENSAT) project.

1.3 Research Objectives

1.3.1 General Objective

The main objective of this research work is to investigate and evaluate water quality for irrigation and drinking purpose in Zamra catchment, Northern Ethiopia.

1.3.2 Specific Objectives

- To analyze and determine physical and chemical water quality parameters for irrigation and drinking purpose.
- To visualize the spatial distribution map of water quality parameters in relation to geology and land use of Zamra catchment.
- To determine the water types and evaluate the suitability of water for irrigation and drinking purpose using FAO and WHO guidelines and Ethiopian Standards.
- To recommend appropriate crops for the study area as per the water quality and to recommend a treatment plan for irrigation and drinking water management depending on the quality criteria.

1.4 Research question

- What are the dominant chemical constituents of water in the study area?
- What is the spatial distribution of the water quality criteria?
- How do geology and land use affect water quality in the study area?
- Where are the most severe water quality problems in the study area?
- Is the water being suitable for irrigation and drinking purposes?

1.5 Research structure

The research is organized into six chapters.

Chapter 1: Presents the introduction of the research work which includes background and justification, research problem, research objectives and research question.

Chapter 2: Describes the literature review which is related to definitions of water quality terms and parameters.

Chapter 3: This comprises the description of the study area. This includes location, physiography, vegetation, climate and drainage system of the study area.

Chapter 4: This chapter presents methods and datasets used to develop the research wok. This includes the collection of secondary data, primary water samples for laboratory analysis, on spot water quality data collection, land use land cover data collection, laboratory analysis.

Chapter 5: This chapter describes results and discussion. This includes the main finding of the research work.

Chapter 6: Presents the conclusion and recommendations made from the research findings.

2 LITERATURE REVIEW

Water is the most important and vital liquid substance to sustain life on earth. It is essential for the survival of life, economic growth and to reduce the food insecurity. Water is used in all sectors and activities such as industrial purposes; irrigation purposes and household use and it is the source of life for living things on earth. It is crucial for the development of urbanization, socioeconomic development, food security and good living standards of human beings (Brhane, 2018; Howladar, Al Numanbakth, & Faruque, 2018; Kahsay et al., 2019; Mandal et al., 2019).

Water can be existing on the surface or groundwater. Surface water includes water in the lake, ocean, pond, spring, dam, and river whereas groundwater occurs beneath the surface of the earth in saturated zones below the water table. The availability of freshwater is limited to a small percentage and this is decreasing with time because of the highly increasing population, urbanization, and high distribution of agricultural extensions. 97.5 % of the surface water is salt water and only 2.5 % is freshwater. Less than 1% of the 2.5 % is accessible for human beings to use.

Surface water is more vulnerable than groundwater for pollution because it is exposed to the surface waste disposal and it is easily accessible for surface pollutants. Groundwater has more complex chemistry than surface water because it passes through different lithologies and routes before it reaches the aquifer, but it is less susceptible to surface pollutants. Groundwater can also pollute through linkage of the industrial and surface pollutants when it recharges from river or other water resources (Freeze & Cherry, 1979; Howladar et al., 2018; Numanbakth et al., 2019). Groundwater is fresh compared to surface water, but it is difficult to remediate if it gets polluted (Anderson, Woessner, & Hunt, 2015).

Water quality is a term used to describe a physical, microbiological, chemical composition, and property of water. To use water for different purposes such as irrigation, human consumption and industrial purposes potable water is required. Water quality has been deteriorated over time due to the increasing industrialization, agricultural extensions, and rapid growth of human population. Knowledge of water quality is crucial in addition to its availability to evaluate its suitability for its specific usage and for monitoring its quality as well its quantity (Brhane, 2018; Dinka, 2016; Mengistu et al., 2019; Numanbakth et al., 2019). Therefore, assessment and monitoring of surface and groundwater quality is preliminary activity before supplying the water for different purposes based on the international and national standards such as for drinking, industrial and irrigation purposes, and other activities. Poor water quality can cause a human health problem, affect the agricultural crop productivity, threat the ecosystem and the environment as well as affects the socioeconomic developments directly or indirectly (Namugize et al., 2018; Shubhra Singh, Raju, & Ramakrishna, 2015).

Water quality can be affected by natural phenomena or anthropogenic/man-made activities. The natural factors that can cause water quality deterioration includes weathering can be chemical or physical weathering due to rainfall and other natural phenomena, evaporation, geology and natural hazards (Chandrasekar et al., 2019). The anthropogenic factors include land use land cover change, fertilizer, urbanization, agricultural developments, waste disposals and industrialization are the main aspects that can cause water pollution. Water quality has a direct relationship with geology or lithological stratigraphy and land use land cover change. The relationship between water quality parameters to LULC and geology is complex and site-specific (Calijuri, Castro, Costa, Assemany, & Alves, 2015; Namugize et al., 2018; Sudhir Singh, Singh, & Mukherjee, 2010).

"The land use land cover change affects geomorphology, soil property, hydrological process and water quality at global, regional and local scales" (Namugize et al., 2018, p. 247). The main factors that change the land use land cover and that can result in the decline of water quality are the conversion of the areas of natural vegetation and green areas to agricultural land, urban, and industrial zones as a result of rapid population growth. The most common physicochemical parameters of water that are mainly affected by land use land cover change are EC, PH, temperature, turbidity, ammonia, nitrate and total phosphorus (Namugize et al., 2018; Singh et al., 2010).

The unwise use of water resource, use of fertilizers to get fertile soil, and use of pesticides leads to the deterioration of water quality (Singh et al., 2010). Plants are selective for the uptake of the nutrients for their growth but if there is an excess concentration of cations and anions in the water and soil this enforces to uptake the heavy metals and other constituents through the root of plants and this can cause threat for their health, failure of crop production and indirectly this affects the human health (Howladar et al., 2018; Ozkay, Kiran, Tas, & Kusvuran, 2014).

The permissible limits of chemical constituents' water and parameters of water quality to use for irrigation, industry and drinking purposes are different. The most important parameters to assess water quality, and to evaluate its suitability for irrigation are Salinity hazard, Sodium adsorption ratio (SAR), percent sodium (%Na), residual sodium carbonate (RSC), Magnesium adsorption ratio (MAR), permeability index(PI) and salinity (FAO, 1985; Nayak & Sahoo, 2014; Sakram & Adimalla, 2018). The presence of trace and heavy metal elements such as Cu, Fe, Mn, Ni, Zn is important in small concentration in water that is used for irrigation to resist the biodegradation and thermal degradation (Mandal et al., 2019).

Alkalinity and PH are related to each other. The higher alkalinity in the water indicates a high concentration of carbonates and bicarbonates and this leads to a high PH of water. Alkalinity is the ability of water to resist PH change that makes the water acidic and this is due to the availability of carbonates, bicarbonates and hydroxides. Water with higher PH value results in the insolubility of calcium and magnesium ions and the solution, water will be dominated by a sodium ion. Higher sodium solution results in permeability problems which can cause salinity hazard in crops (Bekele, Tadesse, & Konka, 2012; Brhane, 2018; Ismail & El-Rawy, 2018; Kahsay et al., 2019; Mandal et al., 2019; Wilcox, 1955).

The chemical parameters such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, CO_3^{2-} SO_4^{2-}, Cl^{-} and physical parameters such as TH, PH, EC, TDS, Alkalinity and salinity are used to assess and evaluate the suitability of water for drinking as well as irrigation purpose. These are common water quality parameters for evaluation of suitability of water for irrigation and drinking purposes (Aghazadeh et al., 2017; Ismail & El-Rawy, 2018; Kahsay et al., 2019; Mandal et al., 2019; Numanbakth et al., 2019; Reimann et al., 2003). The excessive and deficiency of chemical constituents of water can deteriorate the water quality and as a result, it affects agricultural production and human health.

Plants are selective intaking the elements for their growth, however, if there is an excess concentration of the elements, plants can uptake these elements in passive means (FAO, 1985; Ozkay et al., 2014). The main parameters used to assess water quality for irrigation purposes are discussed below.

2.1 Water Quality for Irrigation purposes

2.1.1 Salinity Hazard

The salinity of the water is expressed in terms of the total dissolved solids and electrical conductivity, EC. High values of EC in water indicate that there is a higher concentration of ions and TDS. High salinity in irrigation water causes a problem in the osmotic process in the soil, water stress and a result it affects the water absorptivity plants in the root zones. It is toxic to plants and this leads to salinity hazard and reduction of crop production (Dinka, 2016; FAO, 1985; Kahsay et al., 2019; Tadesse et al., 2009; Wilcox, 1955).

Irrigation water contains dissolved minerals and salts, but the concentration and composition vary depending on the source of water and where it is stored. Both too high and too low concentration of salt reduces water infiltration and crop production (FAO, 1985; Ismail & El-Rawy, 2018).

According to (Wilcox, 1955), irrigation water is classified into four classes based on EC or salinity hazard. These are:

a. **Low Salinity Water (C1):** This type of water can be used for irrigation for most types of crops and in most types of soils without restriction. Leaching is required in areas of low permeability soils. This class of water has an EC value of less than 250 µs/cm.

b. **Medium Salinity Water (C2)**: This type of water is possible to use in areas that have moderate leaching. In such areas that have medium salinity water type, moderate salt-tolerant plants and crops are recommended. It has an EC value in the range of 250 µs/cm to 750 µs/cm.

c. **High Salinity Water (C3):** This is not used in soils that have low drainage. This type of water can be used in soils that have good drainage and it needs special management to control the salinity level. Crops and plants that have a higher level of salinity tolerance should be selected for this type of irrigation water. This type of water has EC value in the range of 750 µs/cm to 2250 µs/cm.

d. **Very high Salinity Water (C4):** This type of water is not suitable to use for irrigation. Under very special cases, this can be used with the high salt tolerance crops and plants under the high permeable soil, high drainage to provide adequate leaching. It has EC greater than 2250 µs/cm.

2.1.2 Sodium Adsorption Ratio (SAR)

SAR is the most important parameter to evaluate the quality of water for irrigation purposes. This indicates the concentration of sodium ion in water relative to calcium and magnesium ions, and it is used to determine sodium hazard. SAR will have a higher value when water contains a higher concentration of sodium ion relative to the concentration of calcium and magnesium ions and this results to have the water higher salinity due to the exchange reaction between Sodium to calcium and magnesium. Accordingly, higher SAR value leads for the potential problem of permeability in the irrigation soil or water infiltration problems (FAO, 1985; Ismail & El-Rawy, 2018; Sakram & Adimalla, 2018).

Like the EC, Wilcox classifies suitability of water for irrigation purposes into four classes based on its SAR property as low sodium water (S1, 1-10 meq/l), medium sodium water (S2, 10-18 meq/l), high sodium water (S3, 18-26 meq/l) and high sodium water (S4, > 26 meq/l) (Wilcox, 1955). As the level of sodium hazard is increasing from S1 to S4 the level of restriction to use for irrigation purposes is also increasing.

It is defined using the following formula (Numanbakth et al., 2019; Wilcox, 1955):

$$SAR\left(\frac{meq}{l}\right) = \frac{[Na^{+}]}{(\sqrt{[Ca^{2+}] + [Mg^{2+}]})/2}$$ …………………………………………………………………… Equation 1

2.1.4 Kelly's ratio

This is also an important parameter to evaluate the water quality for irrigation purposes. This is mainly dependent on the ratio of the major cations of sodium, magnesium, and calcium. Irrigation water is suitable to use if KR is less than one (Ismail & El-Rawy, 2018). This is defined by the following formula:

$$KR\left(\frac{meq}{l}\right) = \frac{[Na^{2+}]}{([Ca^{2+}] + [Mg^{2+}])}$$ --Equation 2

2.1.5 Permeability index (PI)

It is mainly dependent on the concentrations of the major cations and such as sodium, calcium, magnesium and bicarbonate concentrations (Kahsay et al., 2019; Sakram & Adimalla, 2018). It is defined by the following formula:

$$PI\ (\%) = \frac{[Na^{+}] \pm \sqrt{[HCO3^{-}]}}{([Ca^{2+}] + [\ Mg^{2+}] + [Na^{+}])}$$ --Equation 3

Based on this parameter water quality for irrigation is classified into three classes. Class I has PI of greater than 75 % which is suitable for irrigation and indicates excellent water quality, class II has PI value between 25 to 75% and this indicates good water quality for irrigation and class III has less than 25 % value of PI, which indicates unsuitable water quality for irrigation (Kahsay et al., 2019).

2.1.6 Magnesium adsorption ratio (MAR)

MAR is a good indicator to measure the suitability of water for irrigation purposes. The higher percentage of magnesium ratio (>50 %) in water harms crop yield productivity and crop production because it makes the property of water more alkaline by increasing the concentration of alkalinity (Dinka, 2016; Ismail & El-Rawy, 2018; Nayak & Sahoo, 2014). It is defined using the following formula:

$$MAR(\%) = \frac{[Mg^{2+}]}{([Ca^{2+}] + [Mg^{2+}])} * 100$$ ---Equation 4

2.2 Water Quality for Drinking Purposes

The main parameters used to evaluate the suitability of water quality for drinking purposes are physicochemical parameters such as PH, TDS, EC and TH and chemical parameters such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, CO_3^{2-} $SO_4^{\ 2-}$, Cl^{-}. The following table presents the threshold for the evaluation of the suitability of water for drinking purposes from interactions (WHO, 2008) and national (Compulsory Ethiopian Standard, 2013) standards. Water hardness is caused primarily by the presence of calcium and magnesium cations and anions such as carbonates and bicarbonates (Kahsay et al., 2019; Shubhra Singh et al., 2015).

There are standards from WHO and Ethiopian standards for the permissibility of water quality to use for drinking purposes. The threshold values proposed by these two guidelines for different elements is presented in Table 1.

Table 1: Permissible limits to use water for drinking purposes

No	WQ Parameter	Maximum permissible limit (ES, 2013)	Maximum permissible limit (WHO, 2008)
1	PH	6.5 – 8.5	6.5 – 8.5
2	TDS (mg/l)	1000	600
3	EC (µs/cm)	-	750
4	TH (mg/l)	300	500
5	Na (mg/l)	200	200
6	Ca (mg/l)	75	75
7	Mg (mg/l)	50	30
8	K (mg/l)	1.5	
9	Al (mg/l)	0.2	0.2
10	Fe (mg/l)	0.3	0.3
11	Zn (mg/l)	5	5
12	As (mg/l)	0.01	0.01
13	Mn (mg/l)	0.5	0.4
14	Cu (mg/l)	2	2
15	Ba (mg/l)	0.7	0.7
16	Cd (mg/l)	0.003	0.003
17	Pb (mg/l)	0.01	0.01
18	B (mg/l)	0.3	0.5
19	Se (mg/l)	0.01	0.01
20	Cr (mg/l)	0.05	0.05
21	SO42- (mg/l)	250	200
22	Cl- (mg/l)	250	250
23	NO3- (mg/l)	50	50
24	NH3	1.5	-
25	Alkalinity (mg/l)	200	

Source (Compulsory Ethiopian Standard, 2013; WHO, 2008)

The availability of a high concentration of anions and cations in drinking water can cause health problems. The higher concentration of calcium, sodium and potassium, and magnesium ions causes failure of a kidney (Kahsay et al., 2019), hypertension and elevate the blood pressure, and laxative effect for a human being respectively (Kahsay et al., 2019; Sakram & Adimalla, 2018).

There are four groups of water classes based on TDS and TH concentration. Both too hard and too soft water is not desirable for household use (Kahsay et al., 2019). Using water with TDS and TH above the desirable limit results in gastrointestinal irritation and failure of kidney, respectively.

2.3 Geochemical Modelling

Aquachem Geodatabase: Aquachem is a software package that is developed specifically for graphical and numerical analysis of water quality data. It provides a comprehensive selection of different plotting techniques used for analyzing of geochemical data and interpretation of the water quality data. Aquachem database has fully customizable features for chemical and physical parameters of water. Aquachem is used to identify the water types from the piper diagram and the dominant geochemical process using the stiff plot. It also uses for source rock deduction (Hounslow, 1995).

NETPATH model: This is a simple geochemical model. NETPATH model is used to calculate the saturation indices of the mineral phases and saturation of water with respect to different minerals. This indirectly used to determine the mineralogical composition of the groundwater samples.

Saturation index is an indicator used to determine the state of equilibrium of water with respect to mineral phase. This is important to identify the geochemical reaction that controls the chemistry of groundwater and to simulate the geochemical process along the flow paths (Aghazadeh et al., 2017; El Osta, Masoud, & Ezzeldin, 2020). SI less than zero indicates the groundwater is unsaturated with respect to a specific mineral and SI equal to zero specifies equilibrium of water with minerals. On the other hand, SI greater than zero implies the groundwater is oversaturated with respect to a specific mineral and this indicates incapable to dissolve more mineral (Abreha, 2014; Aghazadeh et al., 2017). SI is calculated using the following formula (El Osta et al., 2020).

$SI = log\frac{IAP}{KT}$ ---Equation 5

Where IAP = Ion activity product of the dissociated chemical species in solution

KT = Equilibrium solubility product

3 DESCRIPTION OF THE STUDY AREA

3.1 Location

The study area, Zamra catchment is found in Northern Ethiopia, Tigray regional state, south of Mekelle, (the capital city of the Tigray). Mekelle is found at about 930 km north of Addis Ababa which is the capital city of the country, Ethiopia. Zamra catchment is part of the upper Tekeze basin. On average the distance of the study area from Mekelle city is about 60 km. The study area, Zamra catchment has an area roughly about 1600 km². This covers four specific woredas such as Amba Alaje, Enderta, Huntalo wejerat and Seharti Samre. Geographically it is located between latitudes of 12° 38' 12" and 13° 20' 16" N and longitudes of 38° 59' 23" and 39° 40' 05" E (Figure 1). It is characterized by rugged topography.

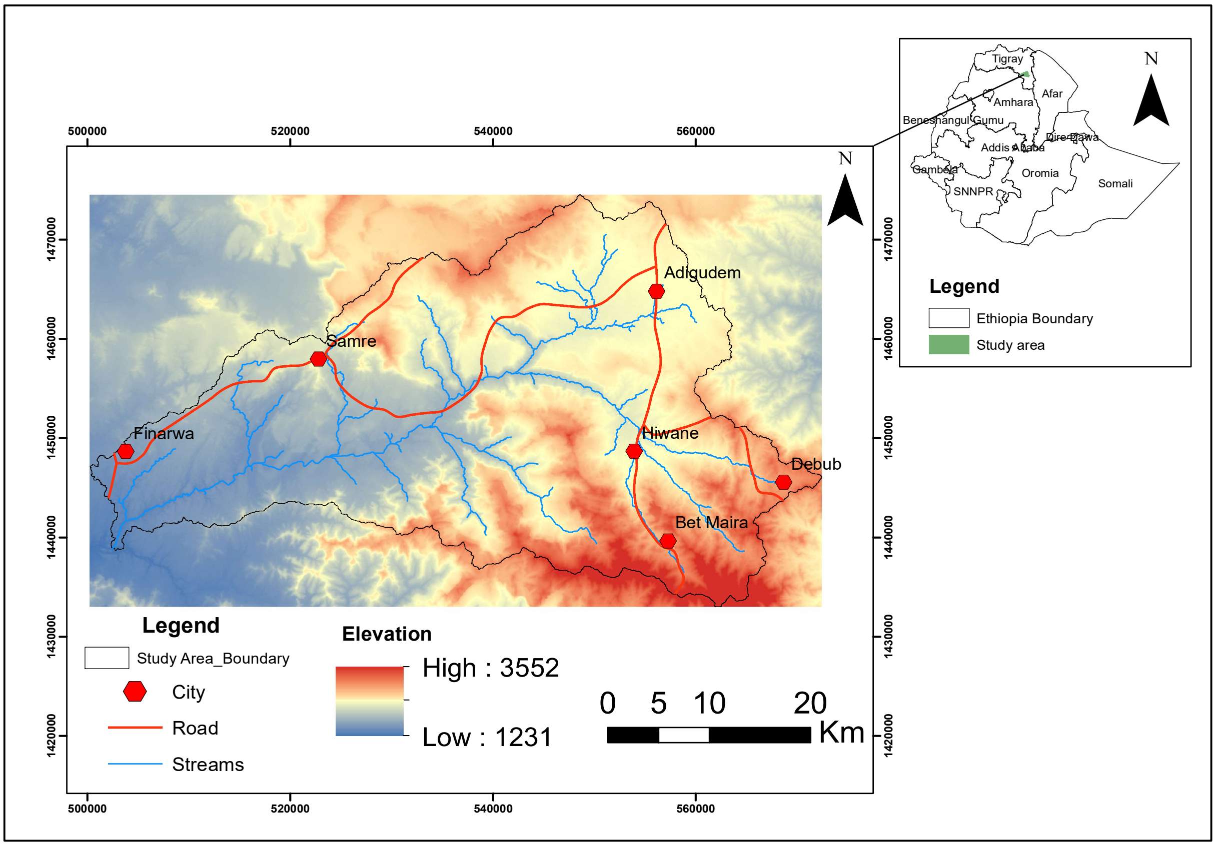


Figure 1: Location map of the study area, Zamra Catchment, Tigray, Northern Ethiopia

3.2 Physiography

The land surface in the study area, Zamra catchment is very rocky and rich in outcrops. The study area is characterized by rugged and cliff topography especially in areas where Adigrat sandstone and the Ethiopian flood basalt are exposed. The northern part of the study area is relatively flat land but in some parts of the study area even it is difficult to access for sample collection particularly in the southern parts such as Amba Alaje, the village of Hiwane. It is characterized by different topographic features such as mountains, hills, cliffs, plateau and valley due to erosional and depositional process. The elevation in Zamra catchment varies from 1231 to 3252 m above the mean sea level (Figure 1).

3.3 Climate

The study area is characterized by a semiarid climate. In Ethiopia there are four seasons called Belg or Autumn includes September, October and November, Baga or Winter includes December, January and February, Tsedey or Spring which includes March, April and May and Kiremt or Summer which includes June, July, and August. There is a bimodal rain season in Ethiopia, as well in the study area Zamra catchment. The study area receives heavy rainfall in the summer season and a little rainy fall in the Bega season whereas the Tsedey is the warmest season (Gebrehiwot & van der Veen, 2013).

The annual average precipitation varies from 450 mm in lowland areas and 970 mm in highland areas. The average temperature varies from 6 ^{0}C in the highlands like Alaje to 35 ^{0}C in the lowlands such as Samre (Girmay et al., 2015).

The climate is variable spatially and temporally with topography and season. There is frequent of drought in the study area. The occurrence of drought is high in the low land parts of the study area. The agricultural sector is more susceptible to the variation in the climate and results in drought and food insecurity. The farming system is then dependent on water from rivers, groundwater, and preserved water on open wells during the dry seasons. There is spatial variation in precipitation and temperature consistent with topography. The intensity and frequency of rainfall are relatively higher in the highland areas than lowland and temperature is vice versa (Abrha & Simhadri, 2015; Gebrehiwot & van der Veen, 2013). The variations in temperature and precipitation in the region is shown below, which studied by other authors (Gebrehiwot & Veen, 2013). The negative value in Figure 2 indicates that drought years and recurrence of drought from 1954 to 2007. The black line is the average of the annual rainfall anomaly and this shows since 1975 drought is increasing. Different studies conducted in the Tigray region indicate that the average rainfall is decreasing with time and temperature is increasing in Tigray (Abrha & Simhadri, 2015; Gebrehiwot & Veen, 2013).

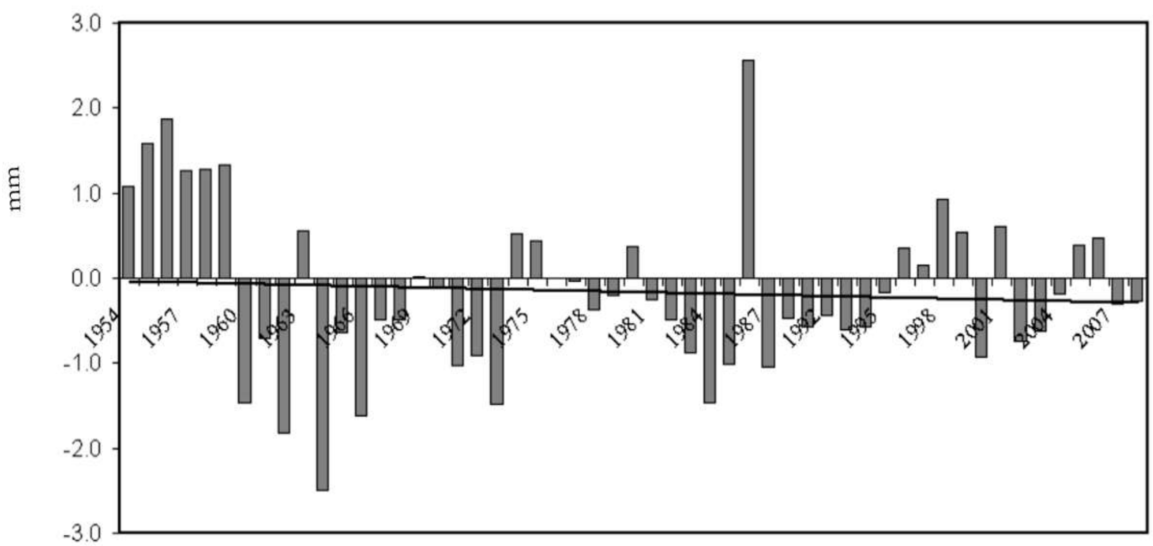


Figure 2: Long-term annual rainfall anomaly (1954 -2008), After (Gebrehiwot & van der Veen, 2013)

3.4 Drainage Pattern

Drainage pattern is a landform that is formed by streams and rivers on the earth's surface (Girmay, 2015). Drainage pattern is governed by the topography of the land, geology, and the gradient of the land. There are several streams in the study area (Figure 3). The dominant drainage pattern of the study area is dendritic.

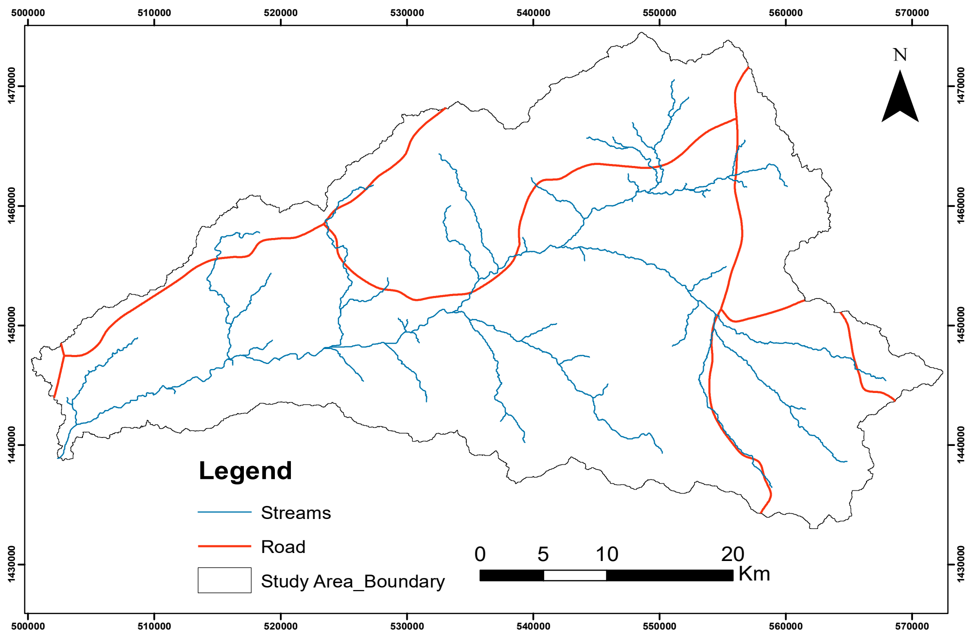


Figure 3: Drainage pattern map of the Zamra catchment

3.5 Vegetation

The study area, Zamra catchment, is covered by agricultural land and sparse vegetation except in some parts which are covered by dense vegetation. As the study area is characterized by rugged topography, then the agricultural land is on the flat land of high lands and lowlands. Some part of the study area is bare land. The most common trees found in the study area are eucalyptus and shrubs.

3.6 Land Use

Land use is a dynamic phenomenon and it changes with time and space due to the anthropogenic activities such as the conversion of an area covered with natural vegetation to agricultural land and urban or other commercial pasture land. Land use land cover change can affect the hydrological process and water quality. Up-to-date land use land cover information is an important input for the management and monitoring of water resources at a local scale (Calijuri et al., 2015).

Land use land cover map is prepared for the study area, Zamra catchment using the Sentinel 2 image (https://scihub.copernicus.eu/dhus), (Figure 11). The main inputs for the land use land cover classification are the Ground truth points collected from the field, Google Earth image interpretation and knowledge of the study area land use.

The classified image is evaluated using the collected ground truth data points. In the field, five (5) classes were identified, but the Built-up class covers a very small area and it is included in the bare land class. Four land use land cover classes were produced for the study area, Zamra catchment. The land cover land use map is produced using a supervised classification method using ERDAS IMAGINE 2020. Accordingly, from the classes in Zamra catchment, Agriculture (rainfed and irrigated) covers the higher percentage, which is 43.55 % followed by Bare land, Forest, and Water respectively (Figure 4).

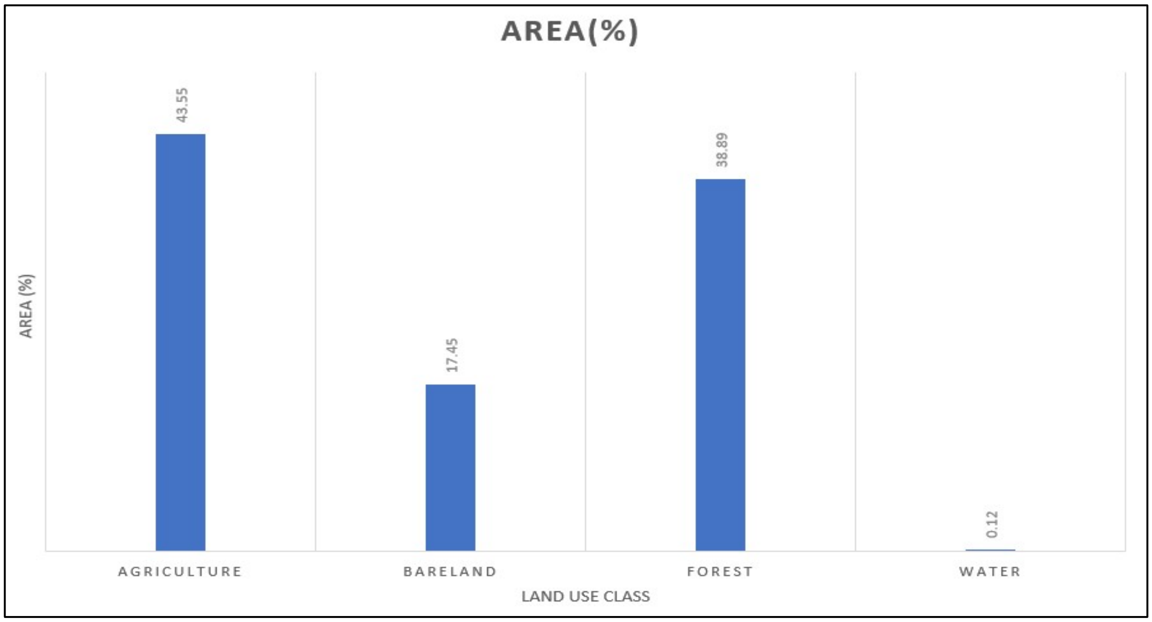


Figure 4: percentage of Land use landcover of the study area, Zamra catchment

3.7 Geology and Hydrogeology

3.7.1 Geology of the Study Area

Stratigraphically, the study area is characterized by the geological formations mainly by Precambrian Basement rock, Enticho Sandstone, Adigrat Sandstone, Antalo limestone, Agulae shale, Amba Aradom Sandstone, Mekelle Dolerite and Ethiopian Flood Basalt(Alaje and Ashenge formations) respectively in order of age from oldest to youngest (Girmay et al., 2015). The study area has a complex geology. The Ethiopian Flood basalt formation dominantly exposed in the southwestern part of the study area. Antalo limestone is exposed in the north part of the study area mostly around Adigudem.

There are geological formations in the study area that are not in a mappable areal coverage, such as shale-limestone intercalations which is along with the contact between shale and limestone.

3.7.2 Hydrogeology of the Study Area

The hydrogeology of the study area is governed by the geological formations, geomorphology, and topography. The different geological formations have different aquifer property which depend on the grain size and composition of the materials. The study area is characterized by highlands topography in the eastern and it decreases towards the west direction where the river water flows.

The water bodies such as rivers and spring decrease their water potential with time during the dry season and even it becomes dry in the late dry seasons (Girmay et al., 2015). Springs are dominantly found in the highlands of Alaje, mainly in the east of the study area.

In the highland, the water level increase and reaches the surface during the summer season and this is an indicator that it recharged directly from precipitation and discharges as spring and it forms marsh area. The main aquifers in the study area are Adigrat sandstone and weathered basalt rocks and yield high potential of groundwater relative to the other geological formations. Adigrat sandstone is the most productive aquifer (Q up to 60 L/s) and Agulae shale is the least productive aquifer.

The occurrence of groundwater in Basalt is mainly related to weathering and geological structures such as joints and fractures (Girmay et al., 2015).

Locally there are soil-water conservation activities from a long time that are mainly implemented to increase the recharge of groundwater, to mitigate soil erosion and to reserve water for irrigation uses like a dam and open wells.

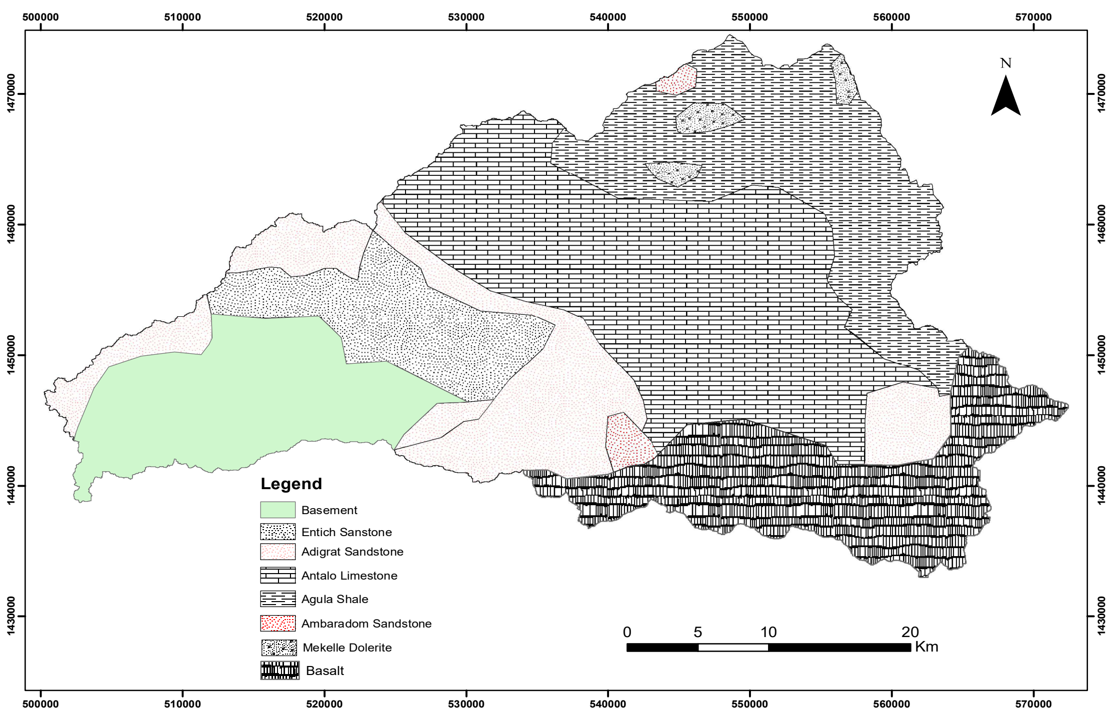


Figure 5: Geological map of the study area, modified from (Girmay et al., 2015)

4 METHODOLOGY AND DATASETS

4.1 Field Data collection

The main objective of the fieldwork is to conduct a detailed survey and use the collected information to create a water quality database incorporating geological, hydrogeological, hydrogeochemical information and to acquire the necessary input data for the Aquachem hydrogeochemical model for the study area, Zamra catchment, Tigray, Northern Ethiopia.

To achieve the general and specific objectives, to come up with reliable results that can answer the research questions primary and secondary data were collected from the study area, Zamra catchment.

4.1.1 Secondary Data Collection

The collection of secondary data was carried out in Mekelle, Tigray regional state, Northern Ethiopia. The distribution of water points, water quality data, hydrogeological data, geological map and lithological logging data are the secondary data collected from different offices for the study area, Zamra catchment. The data was collected from Tigray Water Resource Bureau, Tekeze Deep Water Well Drilling PLC and Relief Society of Tigray. From the collected information's mainly the distribution of water points, geological map and the water quality data were used to identify the places from where to collect the primary water samples. The lithological data, geological map, hydrogeological data were used as additional information to the field survey to prepare the geological map of the study area.

Only 12 water quality data were collected from the secondary data. The statistical summary of the collected secondary water quality data is summarized in Table 2Table 3. The distribution of the water points that have secondary data is shown in

Figure 6. The collected water points from secondary data and physicochemical parameters are attached in the appendix (Appendix I).

Table 2: Summary of water points/scheme with secondary data

No	Type of scheme	Total number
1	Deep well	4
2	River	2
3	Shallow well	2
4	Spring	4
5	Total	12

Table 3: Statistical summary of cations and anions water points having secondary data

No	Parameters	Minimum	Maximum	Average
1	EC (µs/cm)	297	3037.85	1090.32
2	PH	6.72	8.8	7.70
3	Na^{+} (mg/l)	12.8	85.2	43.05
4	Ca^{2+} (mg/l)	45	319	138.92
5	Mg^{2+} (mg/l)	11	61	31.42

6	K^+ (mg/l)	0.3	2.6	1.35
7	HCO_3^-	20	484.43	309.65
8	SO_4^{2-}	7.5	870	269.87
9	NO_3	0	56.7	9.07
10	Cl^-	4	53.4	24.11
11	F^-	0.003	4.1	0.751

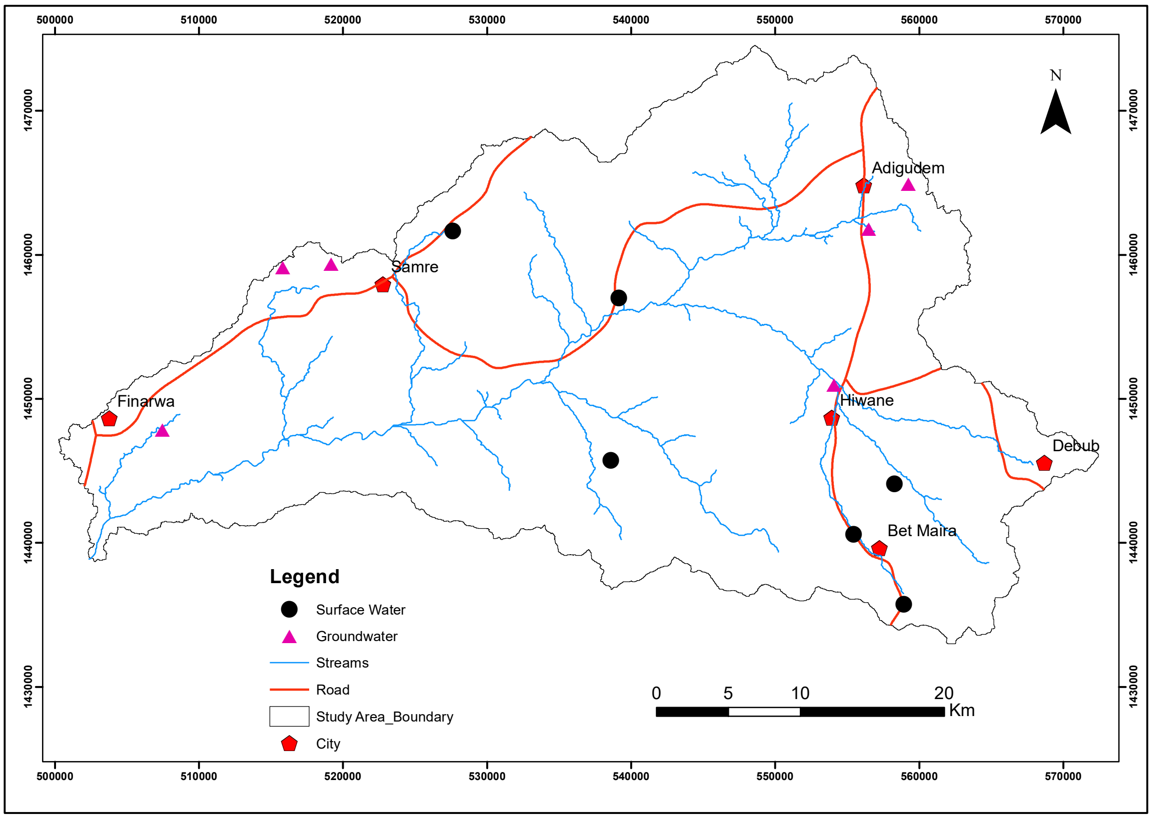


Figure 6: Location map of water points having secondary data

4.1.2 Primary Water Sample Collection and on spot Analysis

To determine and assess the quality and suitability of water quality in the study area, Zamra catchment representative water samples were collected from the selected points. The information collected from the secondary data such as the distribution of water points, geological map and the water quality data were used to identify the representative areas from where to collect the primary data of water samples. Besides this, the geological formation/rock type, type of scheme and its application either for drinking or irrigation purposes are also used to identify the representative areas. The fieldwork was conducted from January 13, 2020 to February 08, 2020.

The representative water samples were collected from different schemes of groundwater and surface water. The water samples from groundwater such as deep wells, shallow wells and hand-dug wells were collected after pumping the wells for about 15 minutes to remove the stagnant groundwater, and to get a fresh sample of water that represents the water point. The sampling method for the groundwater is depth-integrated because the water sample is collected from wells that are already functional.

Whereas the sample from the surface water (mainly river and canal) which are used for irrigation purposes were collected at different parts of the river and canal, at the upper and lower part of the river to determine the effect of land use such as farmlands or agriculture, fertilizer on water quality. The water sample from surface waters (mainly springs) which are used for drinking purposes were collected from their source.

Before filling the bottles with the water samples for analysis, the bottles were cleaned by rinsing with distilled water followed by the water samples. The water samples were filtered by a 0.45 μm pore size membrane filter to remove the suspended particles and microorganisms before acidifying. The samples are collected using the standard method (EPA, 1982).

Totally 120 water samples were collected for chemical analysis in a laboratory from sixty water points, two samples per water point. From the collected water samples, 60 of them were acidified by HNO_3 for cation analysis and 60 water samples were acidified by HCl for anion analysis to prevent the chemical constituents from precipitation and adsorption to the wall of the container and reduce the bacterial activities.

The water samples were collected from different scheme types such as deep well, hand-dug well, shallow well, open well, canal, river, spring, dam and check dam.

Some of the physicochemical parameters were measured on the field parallel to the collection of the primary water samples. This includes the hydrogen ion concentration(PH), electrical conductivity (EC), dissolved oxygen (DO) and temperature which are measured using HQ40d multimeter. The measurements were done by calibration of measuring tabs using the liquids which are available with the HQ40d multimeter for each of the parameters. The constituent of total dissolved solids of the water samples has been calculated from the on-spot measurement of EC. The concentrations of chloride, alkalinity and total hardness are also measured using a standard titrimetric method on the field parallel to the primary water sample collection. Color and odor are tested on the field by eye observation. And the result indicates that except for the open wells which show green color all water samples collected from groundwater and surface water are colorless and odorless. This is because the sample was collected in the dry season. The method that is used for field data collection is shown in Figure 7.

The sample bottles were filled with water samples, tightly capped, labeled properly and water samples were preserved in the refrigerator in the ITC geoscience laboratory until the samples go for analysis of cations and anions. The statistics physicochemical parameters measured in the field are summarized in Table 4.

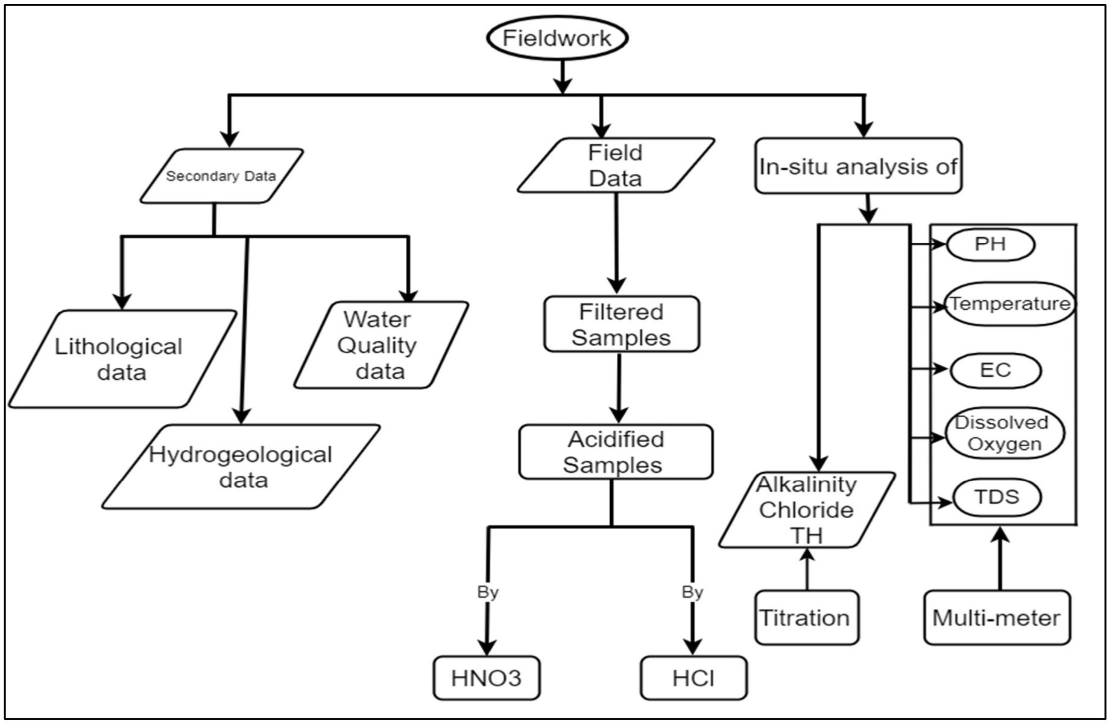


Figure 7: Flow chart of field data collection, primary and secondary data

Table 4: Statistical Summary of the parameters measured in the field

No	Parameters	PH	EC	TDS	DO	Alkalinity	Chloride	Hardness	Temp.
	Unit		µs/cm	mg/l	mg/l	mg/l	mg/l	mmol/l	^{0}C
1	Maximum	10.4	5040	3276	18.6	1300	570	13.5	28.4
2	Minimum	6.83	112	72.8	1.01	110	10	0.5	16.8
3	Average	7.75	926.18	602.02	4.39	606.33	49.95	3.90	22.83

Figure 8: Photos that show field data collection, water sample, based on scheme type

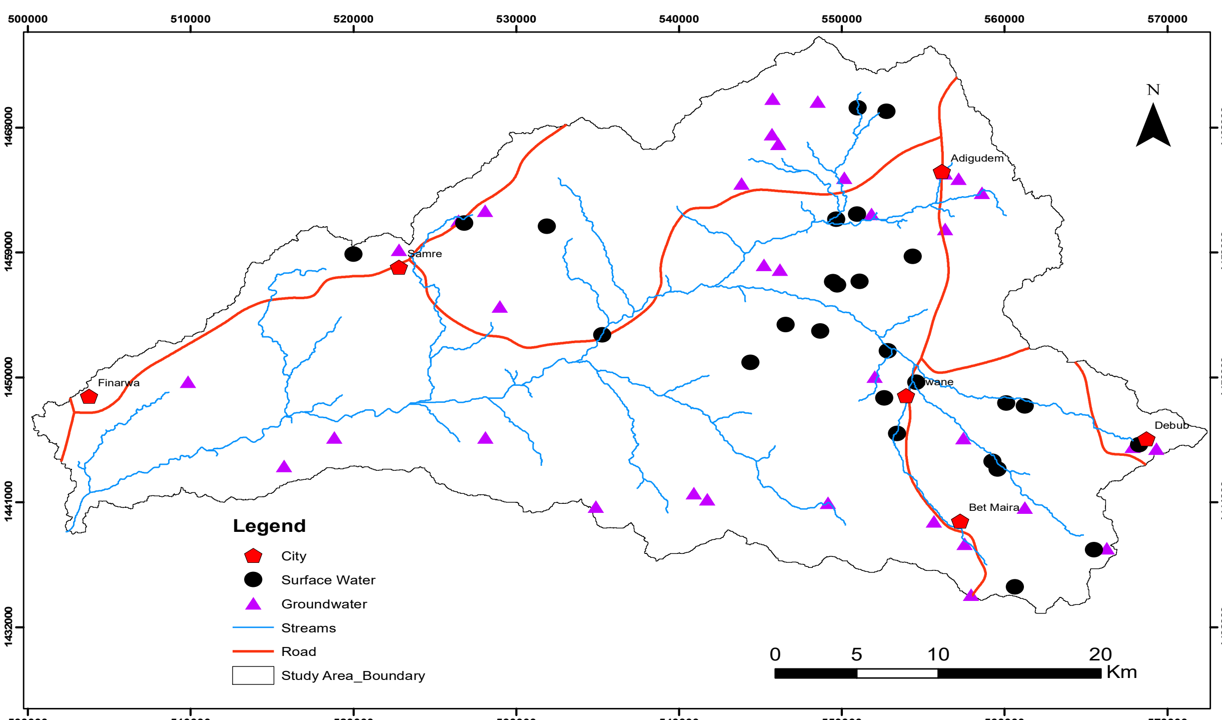


Figure 9: Location and distribution of primary collected water points, Zamra catchment

4.1.3 Land Use Land Cover Ground Truth Data Collection

Ground truth data for land use land cover classification were collected from the study area, Zamra catchment using GPS and digital camera. Totally 156 observations points were collected for LULC classification and verification of the classified image. Out of these observations 46 for Agricultural land (rainfed and irrigated), 50 for Bare land, 35 for forest and 25 for water classes were collected. Half of the collected points are used for classification and the others are used for evaluation of the classified image from sentinel 2 using the standard ERDAS IMAGINE 2020.

LULC map is produced for the study area, Zamra catchment using the https://scihub.copernicus.eu/dhus Sentinel 2 image of October 26 and 29 (Figure 11). 9 bands such as band2 -8, band11 and 12 are used for image classification. The classified image was assessed its accuracy using the ground truth points collected from the field. 83 ground truth points were used for the accuracy assessment. The classified image is assessed its accuracy using the confusion matrix in ILWIS. The result of the accuracy assessment is presented in Table 5. The accuracy result is accepted from the view of the use of the LULC map for this purpose.

Table 5: Error matrix

Classification result (i.e. classified image to be evaluated)							
Reference data		Agriculture	Bare land	Forest	Water	Row Total	User Accuracy (%)
	Agriculture	20	5	10	1	36	55.56
	Bareland	0	19	2	0	21	90
	Forest	5	1	6	0	12	50
	Water	0	0	0	14	14	100
	Column Total	25	25	18	15	59	
	Producer accuracy (%)	80	76	33.33	93.33		
	Overall Accuracy (%)						71.08
	Overall Kappa statistics						0.5902

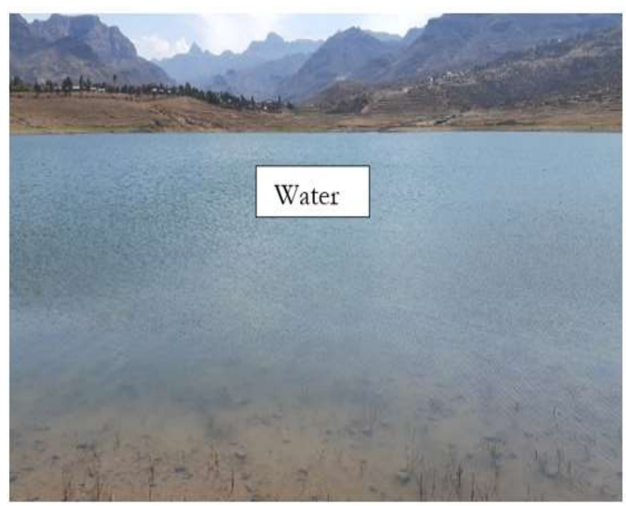


Figure 10: Photos collected for LULC from the study area, Zamra catchment

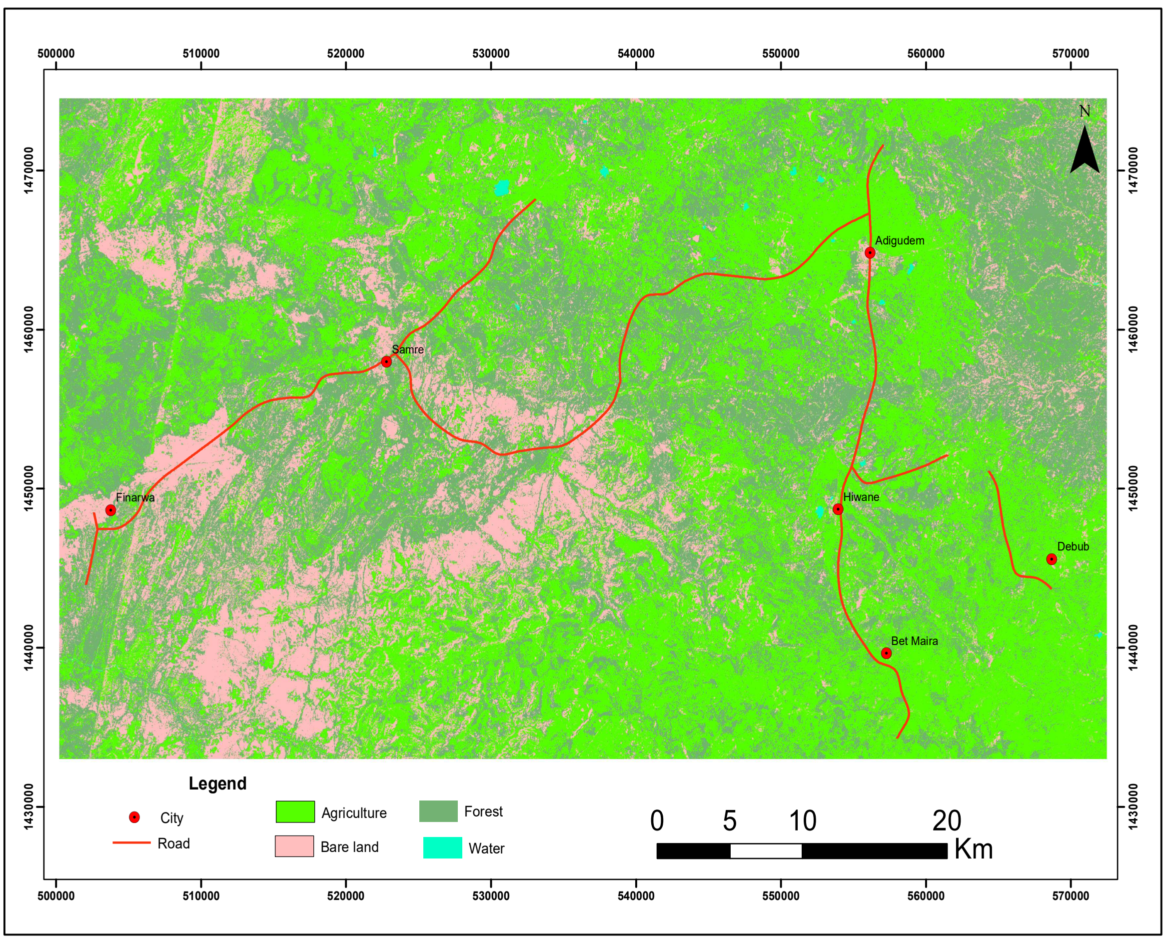


Figure 11: Land use land cover map of Zamra catchment

4.2 Laboratory Analysis

The representative water samples collected from the study area, Zamra catchment from different scheme types which are used for irrigation and drinking purpose for analysis of cation and anions were analyzed for their physical and chemical parameters. The physicochemical parameters such as PH, EC, dissolved oxygen, total hardness, alkalinity and chloride are analyzed in the field parallel to the primary sample collection. The collected water samples were preserved in the refrigerator in the ITC geoscience laboratory until the samples go for cations and anions analysis.

The chemical parameters of the water samples such as cations, sulfur, phosphorus and silicon were analyzed from the water samples which are acidified with nitric acid using Inductively coupled plasma - optical emission spectrometry (ICP-OES) in the ITC Geoscience Laboratory. The laboratory analysis of cations was carried out after the water samples got enough liquified. Out of the sixty collected water samples, 33 water samples that have a composition the major cations that are above the detection limit of the ICP-OES are diluted with the ratio of 1 to 10 of water sample and ultrapure water, respectively. The ICP-OES is settled to measure three times for one parameter and the value with the low residual standard deviation (RSD) is taken.

The anion composition of the water samples such as SO_4^{2-}, NO_3^- and NH_3 was determined from the water samples which are acidified using HCl using the HACH DR3900 Spectral Photometer instrument, in ITC Geoscience laboratory. For the anion analysis out of sixty collected water samples, 24 water samples were diluted. Out of these 24, 23 water samples are diluted with the ratio of 1 to 10 and 1 water sample with the ration of 2 to 20 of water sample and ultrapure water, respectively. The dilution of the water samples was required for the water samples that have a higher concentration than the detection limit of the instrument, HACH DR3900 Spectral Photometer.

To measure the concentration of anions using DR3900, the water samples must be at room temperature and a PH of 7, neutral water. The water samples were acidified using HCl to PH of 2 at the time of sample collection to prevent the anion constituents from precipitation and adsorption to the wall of the container and to reduce the bacterial activities. NaOH solution is used to neutralize the water samples. For the analysis of the anions, different powder of reagent chemicals was used. These include Ammonia Salicylate and Ammonia Cyanurate for Ammonia, NitraVer 6 Reagent, and NitriVer 3 Reagent for nitrate and SulfaVer 4 powder for sulfate. The Water samples without the adding of the powder reagents are used for calibration of the instrument. The standard methodology given by the HACH DR3900 website for determination of the specific anions is used during the analysis.

The results from the analysis are used to determine the status of the water quality in the study area related to geology and land use land cover and this is also used to prepare input data for the hydrogeochemical model, Aquachem. The statistical summary of the analyzed major cations and anions is given in Table 6.

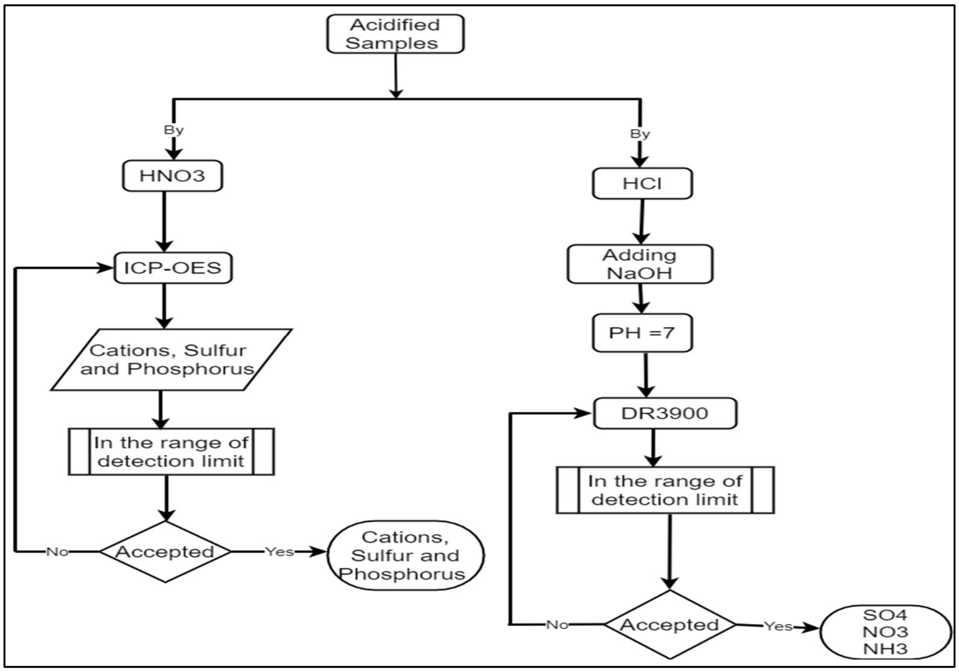


Figure 12: Flow chart laboratory analysis

Table 6: Average, maximum and minimum values of major cations and anions of the study area, Zamra catchment

No	Parameters	Unit	Minimum	Maximum	Average
1	Ca^{2+}	mg/l	1.94	484.75	111.94
2	Mg^{2+}	mg/l	1.46	148.63	39.72
3	Na^{+}	mg/l	5.68	806.78	64.54
4	K^{+}	mg/l	0.0028	15.084	2.65
5	Al^{3+}	mg/l	0.0024	0.0109	0.0042
6	Mn^{2+}	mg/l	0.0016	0.248	0.020
7	Fe^{2+}	mg/l	0.020	0.491	0.084
8	HCO_3^{-}	mg/l	0	793	350.85
9	CO_3^{2-}	mg/l	0	72	6.6
10	SO_4^{2-}	mg/l	2	1360	148.67
11	NO_3^{-}	mg/l	0	1.3	0.311
12	Cl^{-}	mg/l	10	570	49.5

4.3 Charge Balance Error (CBE)

To evaluate the accuracy of the chemical analysis results the reliability of the anion-cation electroneutrality is checked (Equation 7). The chemical analysis is acceptable if the CBE value of the cation-anion balance is less than 5 %. It is also possible to accept the value of CBE up to 10 % depending on the analyzed parameters (Kahsay et al., 2019).

$$CBE = \left(\frac{\Sigma cations - \Sigma anio}{\Sigma cations + \Sigma anio}\right) * 100 \quad \text{------ Equation 6}$$

61.67 % of the collected samples have CBE of less than 10 %. And 38.33 % of the water sample has greater than 10 % of the charge error balance (Appendix IV). This is because the anion parameters were analyzed only for some parameters and the analysis of the anions was carried out after long time preservation of the water samples. This can also happen if the samples are diluted. In some of the water samples, there are negative values of CBE. The negative value of CBE is an indicator that anions are abundant than cations (Brhane, 2018).

4.4 Hydrogeochemical Analysis

Aquachem 2014.2: The results of the chemical analysis of anions and cations are plotted and interpreted using Aquachem 2014.2 software. Aquachem is used for graphical presentation and interpretation of water quality data, to identify water types. The ternary and piper plots are used to identify the major cation distribution and to determine the water types, respectively. Wilcox diagram (Wilcox, 1955) is used to plot and classify water quality based SAR (alkali hazard) and EC(salinity hazard).

Source rock deduction: This is used to determine the origin of the water samples geochemically. Originally, the source of groundwater is rainfall, and which is relatively in good quality. But when water passes through porous material before it reaches the groundwater its composition will be altered by rock-water interaction, weathering, and evaporation, and ions such as Ca, Mg, SO4, and SiO2 will add to the water (Hounslow, 1995). Source rocks are deducted using the ionic ratio method.

NETPATH model: NETPATH model is used to calculate the saturation indices of the mineral phases and saturation of water with respect to different minerals for the water samples collected from Zamra catchment. The results of the chemical analysis of anions and cations for the calculation SI in NETPATH model. SI is calculated using the following formula (El Osta et al., 2020).

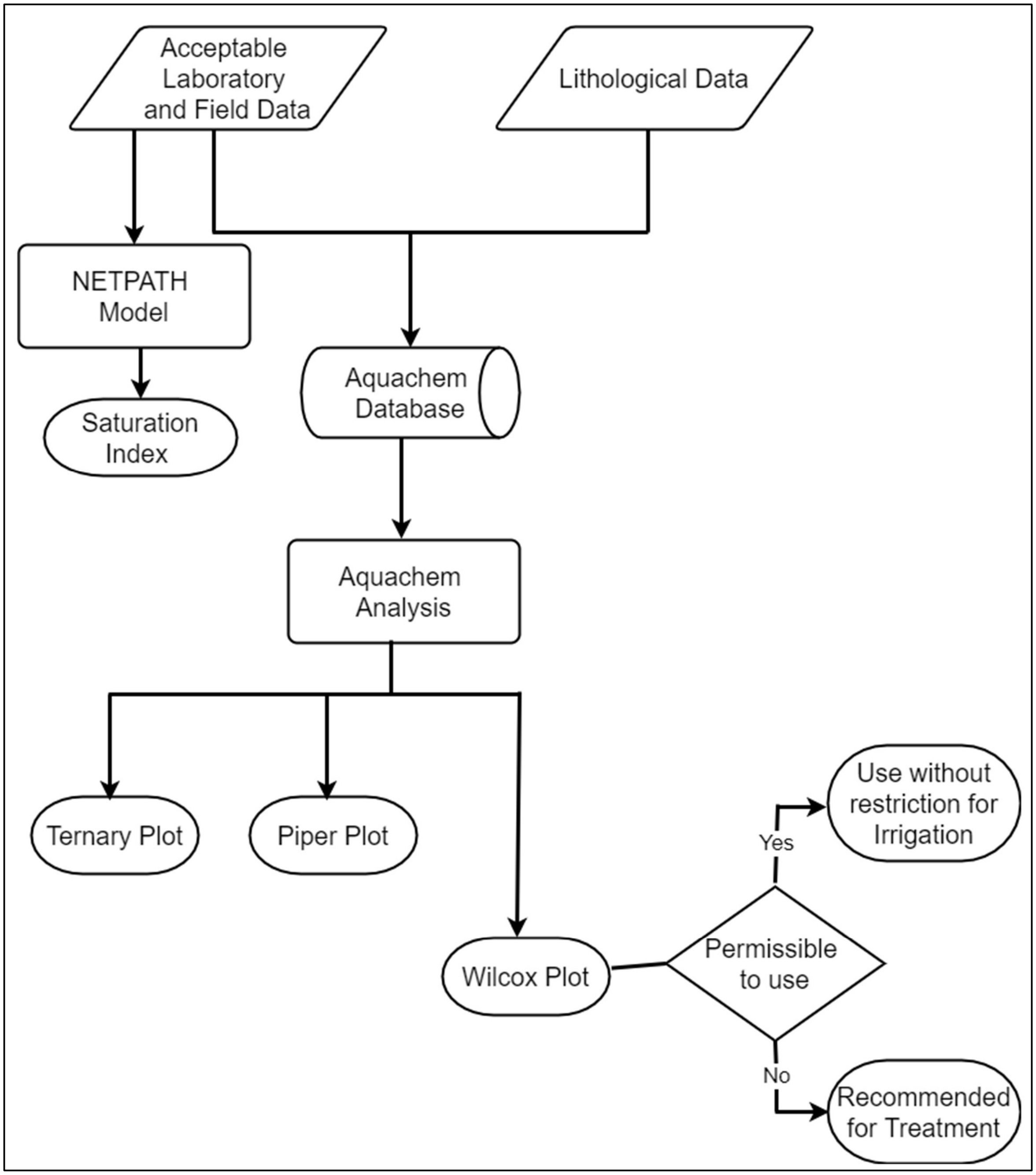


Figure 13: Flow chart of hydrogeochemical analysis using Aquachem

4.5 GIS Analysis

The spatial distribution of water quality related to geology and LULC is visualized. Water quality parameters are entered into the geological map and LULC map to see the difference in the concentrations on the map in relation to geological formations and LULC.

Descriptive statistics is used to determine the relationship between geology and land use. The water samples from the same geology and LU are identified using the ARC GIS, intersect tool. This tool used to identify the water samples that are collected from the same geology and LU. Then the average of the WQ parameters is considered to analyze the relationship between WQ parameters to Geology and LULC.

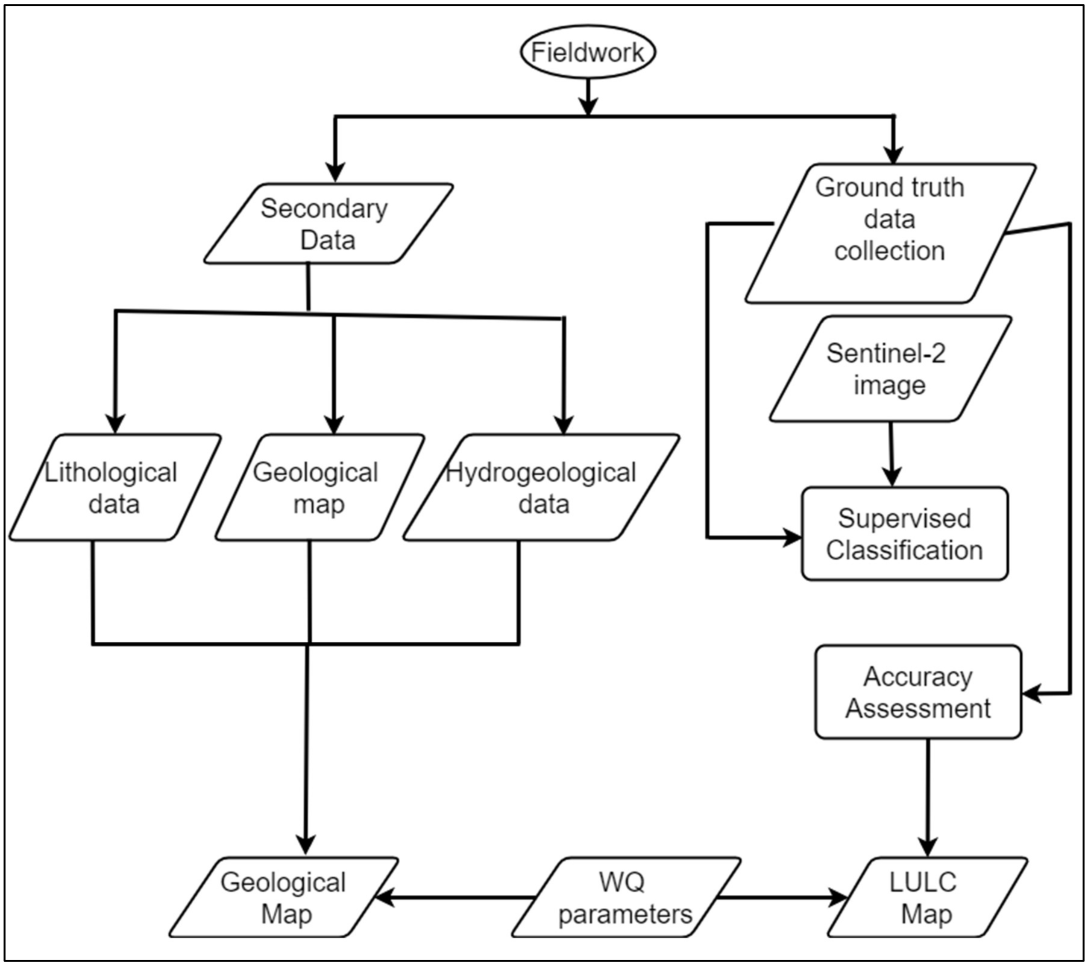


Figure 14: Flow chart of visualizing WQ VS geology and LULC map

5 RESULT AND DISCUSSION

The result of the chemical analysis indicates that the chemical composition of water samples is different in geological formations, scheme types, and elevation. There is a spatial variation of the chemical compositions of water samples even for the samples that are collected from the same geology and scheme type. This is an indicator that the water quality is not dependent only on one factor rather it depends on elevation, scheme type, elevation, and LULC. The result of the chemical analysis for cations and anions is presented in Appendix III.

5.2 PH, EC, TDS, and TH

The PH of the water samples collected from the study area, Zamra catchment varies from 6.83 to 10.4. The highest PH is observed in the water samples collected from the dam which is constructed around the village of Hagere Selam on Agulae shale rocky type. The high PH can be due to the surface pollutants from the village.

Electrical conductivity and TDS are found in the study are between 112 µs/cm to 5040 µs/cm and 72 mg/l to 3276 mg/l respectively. SHW19 shows higher concentrations of the chemical constituents than the other water samples. The sample is collected from Agulae shale rock type and used for and it is found near Adigudem city. The reason for higher chemical constituents can be pollution arises from the city. Agulae shale has high porosity but low permeability. And then the pollutants cannot easily travel through the pore spaces to another place. From the secondary collected water quality data, DW1 has EC of 3037.85 µs/cm which is also collected from Agulae shale.

The total hardness in the study area varies from 50 mg/l to 1350 mg/l. TH is caused mainly by the presence of calcium, magnesium, carbonate, and bicarbonates. Higher TH is observed in SP8 which collected from Antalo limestone

The variation of the physicochemical parameters is not only dependent on geological formation, but it also varies with scheme type and elevation. Even water samples collected from the same geological formation shows the variation in the chemical composition water.

Figure 15 presents some examples to show the variability of the composition of water in different geological formations, scheme type, and elevation. The concentration of the physicochemical parameters is increasing as elevation decreases. Water moves from high altitude to lower part and there is less probability for log residence time.

In general, the higher concentration of EC, TDS and TH is found in Agulae shale and it decreases from Agulae shale > Antalo limestone > Basement > Basalt >Adigrat sandstone > Amba Aradom sandstone respectively. The concentration of EC, TDS, and TH is higher in shallow wells and surface water (river, canal, and spring than the other scheme types.

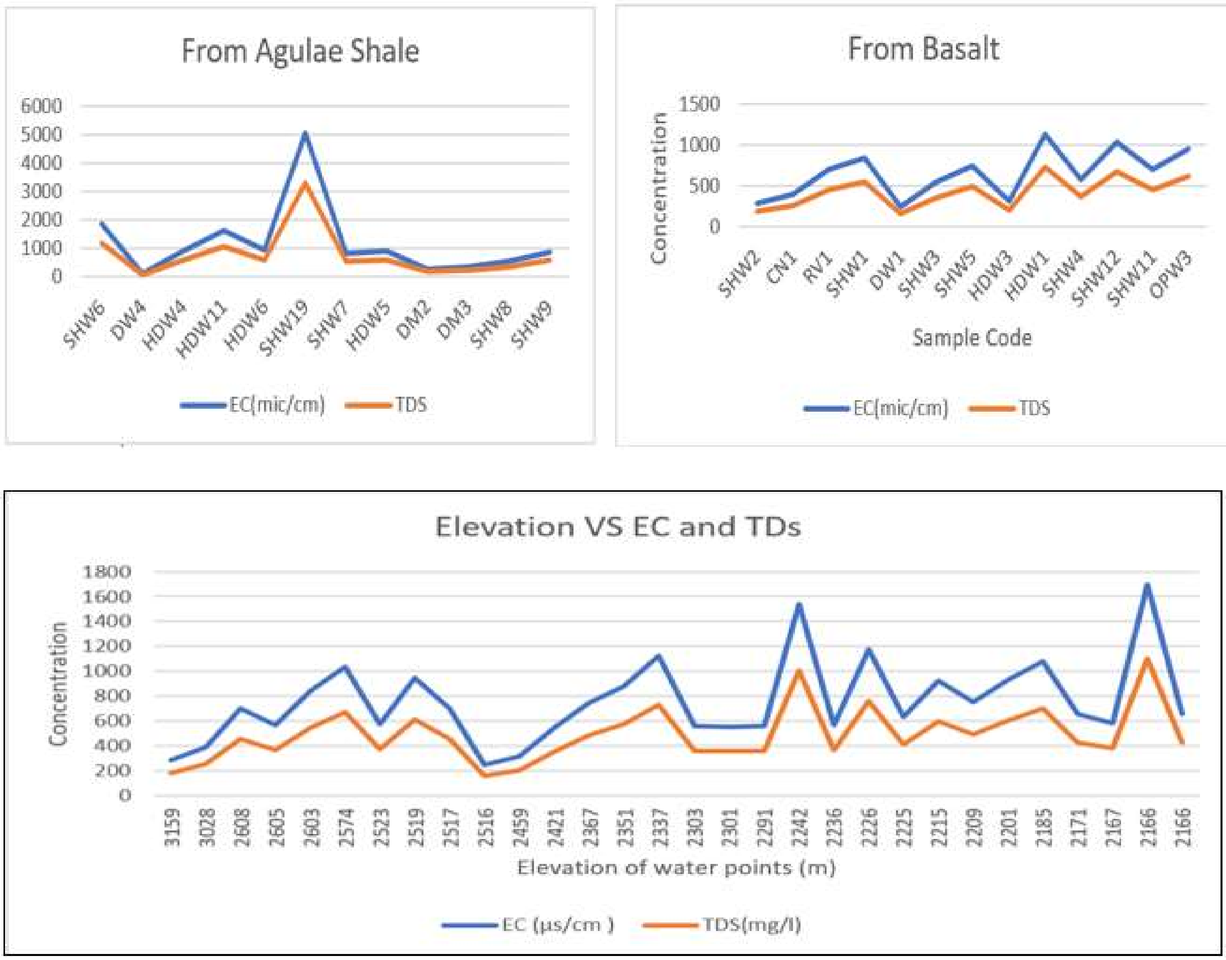


Figure 15: Variability of TDS and EC with geology, elevation and scheme type

5.3 Cations and Anions

5.3.1 Cation concentrations

Calcium is the most dominant major cation in the study area followed by sodium, magnesium and potassium cations, respectively

Calcium concentration is found between 1.94 mg/l to 502 mg/l, with an average of 111.94 mg/l. The higher concentration of calcium is observed in SHW6 which is collected from Agulae shale exposure, DW3, and SP8 which are sampled from the lithology of Antalo limestone. Higher calcium concentration is due to the dissolution of calcite and gypsum minerals (Sheikhy Narany et al., 2014; Yang et al., 2016).

The concentration of sodium in Zamra catchment is in the range of 5.68 mg/l to 175.9 mg/l for 98.33 % of the water samples. Only the water sample collected from SHW19 has 806.78 mg/l concentration of sodium. A higher concentration of sodium ion is possibly due to the leaching of clay minerals and ion exchange (El Osta et al., 2020).

The concentration of magnesium ion in the study area ranges from 1.46 mg/l to 148.63 mg/l with an average concentration of 39.72 mg/l. A higher concentration of magnesium is found in SHW15 and

SHW19. SHW15 is collected from basement rock. It is located at the contact between Adigrat sandstone and basement rock. Weathering is high along with the contact and this can be the reason to have a high concentration of Mg ion. A higher concentration of magnesium can be due to water-rock interaction. The concentration of potassium ion ranges from 0.0028 mg/l to 15.08 mg/l with an average concentration of 2.65 mg/l. A higher concentration of K ion is found in SHW14 and SHW14 which are collected from Basement exposure and SHW17 which is collected from Adigrat sandstone. The higher concentration of K is due to weathering of potassium feldspar minerals and it can also result from fertilizers. The other cations are found as minor and trace elements (Appendix III).

The concentration of major cations is higher in shallow well and surface water than in deep wells. The reason for high chemical constituents in the surface water can be its susceptibility to surface pollutants. And for shallow wells, during the drilling of shallow wells, there is no any cementation for the layers that can lower the water quality, which is applicable for deep well during the drilling procedure. Shallow wells are drilled relatively higher depth than hand-dug wells and mixing of water from different layers is also expected. This can be the reason to have high concentrations in shallow than the deep well and hand-dug well.

A higher concentration of cations is observed in water samples collected from Agulae shale and the low concentration is recorded in water samples from Mekelle dolerite. The reason for the high concentration of the cations in Agulae shale is due to its high porosity but low permeability nature. Geology is also the main factor in the variability of water quality.

The concentration of cations is also decreasing with an increasing elevation of sampled water points (Figure 16).

5.3.2 Anion Concentrations

The dominant anions are bicarbonate, sulfate, and chloride, respectively. Bicarbonate and carbonate concentration are found in the range between 0 to 793.208 mg/l and 0 to 150 mg/l respectively. High bicarbonate is recoded in water samples collected from Basalt. This is can be due to weathering of silicate minerals. The concentration of sulfate varies from 2 to 1360 mg/l. Chloride concentration is found between 10 mg/l to 570 mg/l. The highest chloride concentration, 570 mg/l is recorded from SHW19 which is collected from Agulae shale. The other water samples have less than 210 mg/l of chloride concentration even samples collected from the same lithology as SHW19.

Bicarbonates are found in high concentrations in water samples collected from Basalt terrain. This can be due to the weathering of silicate minerals which are abundant in basalt rocks. DW3, SP8, and CD1 show a high concentration of sulfate which is collected from Antalo limestone and HDW1 which is sampled from Basalt exposure. The high concentration of sulfate can be due to the dissolution of gypsum.

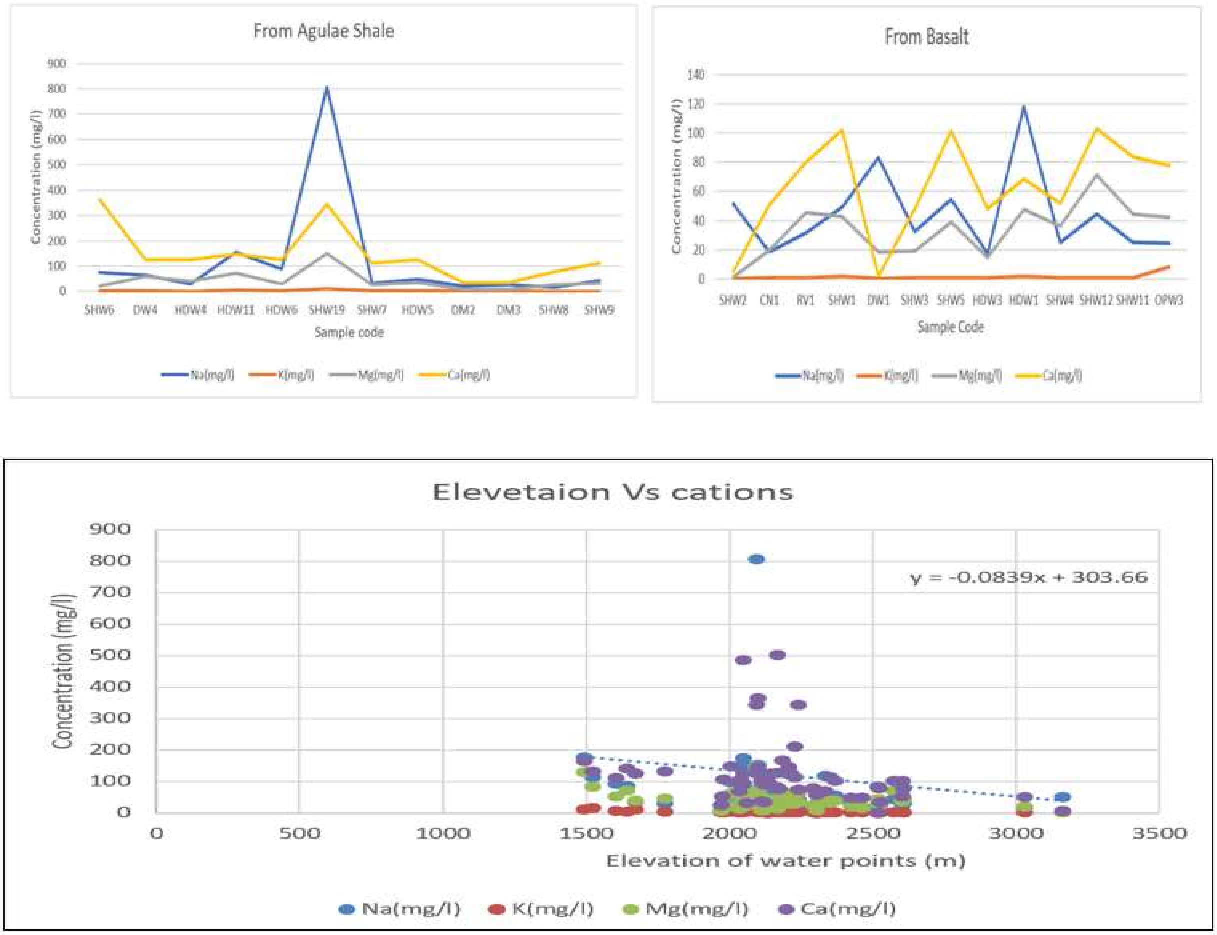


Figure 16: Spatial variation of cations with geology, elevation and scheme type

A high concentration of anions is recorded in water samples collected from surface water and shallow well than the other scheme types. Surface water is easily accessible for pollutions raised from the environment and this can the reason for the abundance of anions in surface water.

On average, the highest concentration of anions is recorded from the water samples collected from Antalo limestone. The occurrence of high concentration for carbonate and sulfate ions in shallow wells can be due to the dissolution of calcite and gypsum minerals, respectively.

The concentration of anion is also decreasing as elevation decreases (Figure 17). The reason for this can be groundwater is flowing faster in the high altitudes than the low altitudes which is related to the head hydraulic head of water. And water passes many routes to recharges the aquifers found in low altitudes. Because of rock-water interaction in the flow paths, it can be also a reason to have high chemical constituents for water points found in low altitudes.

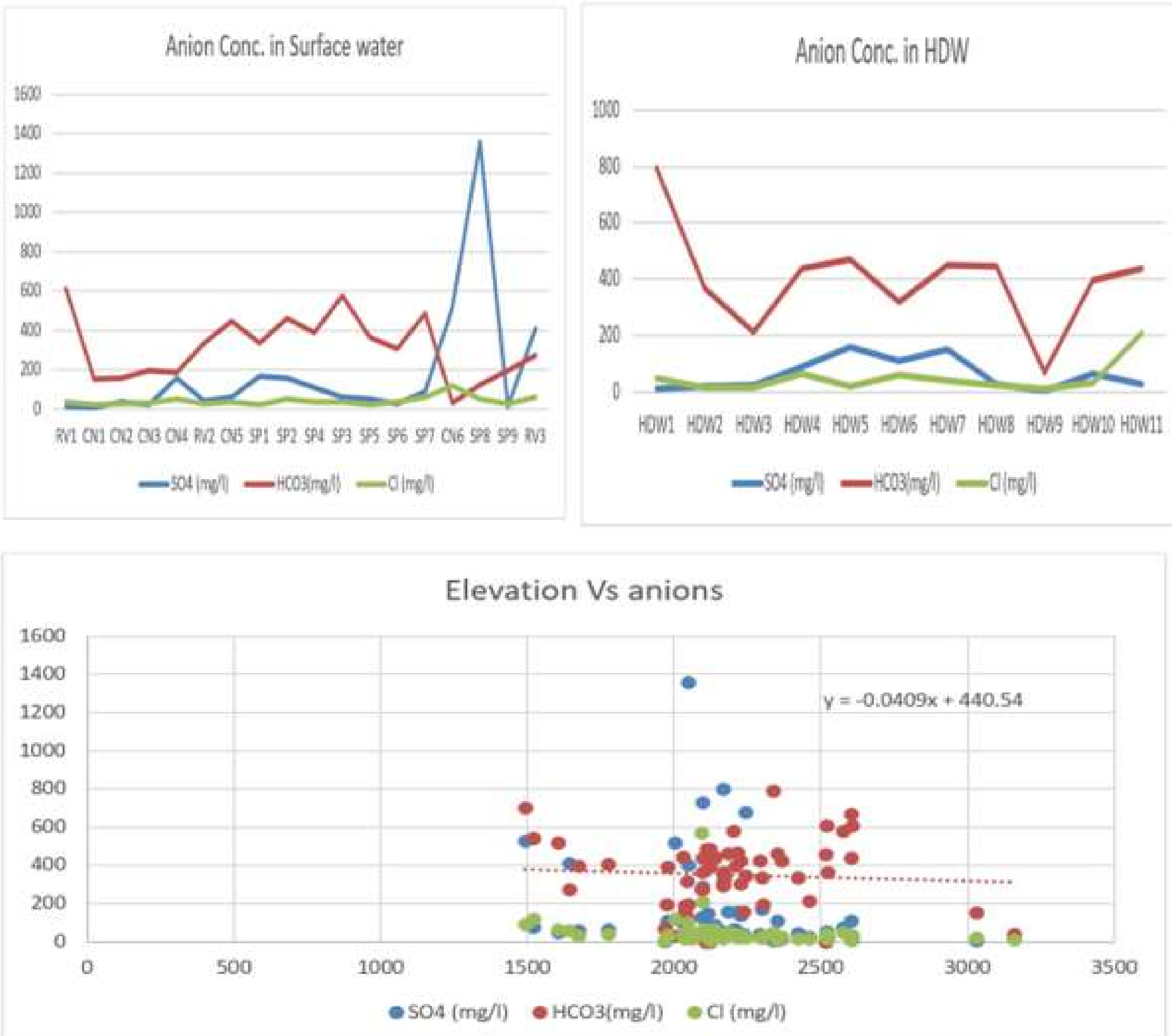


Figure 17: Spatial variation of anions with geology, elevation and scheme type

The higher concentration phosphorus, ammonia, and nitrate is recorded in water samples collected from the agricultural land. This can be happening because of fertilizer and pesticides used in agricultural lands.

The spatial variation of the chemical constituent of water is not dependent on only geology, land use, elevation, or scheme type. All of these elements are a valuable factor in water chemistry.

5.4 Hydrogeochemical Facies

The hydrogeochemical facies is a term used to describe bodies of groundwater in an aquifer that are different in chemical composition (Chandrasekar et al., 2019; Kahsay et al., 2019). There are different methods used for the interpretation of the hydrogeochemical facies of water.

5.4.1 Identification of Water Types Using Piper diagram

The piper diagram is used to determine the water types (Piper, A.M. (1953). The piper diagram consists of two triangular-shaped fields to plot the cations (lower left side) and anions (lower right side) in separate plots and one diamond-shaped filed to plot the matrix transformation of cations and anions (Kahsay et al., 2019). Aquachem 2014.2 version software is used to produce the piper trilinear diagram for Zamra catchment.

The result of the piper plot indicates that the dominant water type is magnesium bicarbonate (Figure 18). Most of the water samples show that Na-Mg-Ca-HCO3 water type with some extent of Ca-HCO3-SO4. There are chloride and bicarbonate chloride water types near to Adigudem city. As stated by (Chandrasekar et al., 2019) the presence of chloride in the groundwater is due to the leakage from the waste disposals, dissolutions of halite, and other related minerals. The upper Zamra catchment is dominated by the bicarbonate water type and this is an indicator of young water and short residence time. The hydrochemical water type of the study area is presented in Appendix IV.

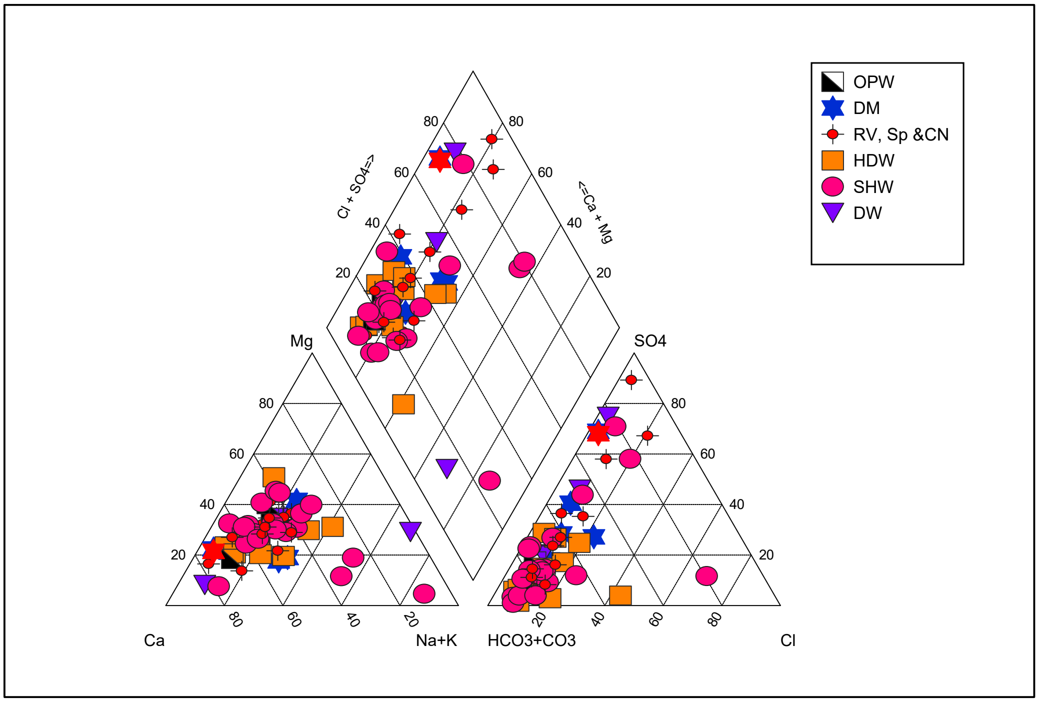


Figure 18: Piper plot showing water types for the water samples, Zamra catchment

(Where OPW= open well, DM=dam, RV, SP and CN = river, spring, and canal, HDW=hand dug well, SHW=shallow well and DW = deep well).

5.4.2 Source Rock Deduction

The ionic ratio is used to determine the geochemical processes that govern groundwater chemistry (Mallick et al., 2018; Numanbakth et al., 2019; Sheikhy Narany et al., 2014; Vinograd & Porowski, 2020; Yang et al., 2016). The ratio calculated to determine the geochemical process for the study area, Zamra catchment is presented in Appendix V.

The abundance of Ca and Mg ions in groundwater is related to either dissolution of carbonate rocks or weathering of silicate minerals. The ratio of Ca^{2+}/Mg^{2+} is used to differentiate between the dissolution of dolomite, calcite, and weathering of silicate minerals (Sheikhy Narany et al., 2014). The ratio of Ca^{2+}/Mg^{2+}

less than one indicates that the dissolution of dolomite, between one and two dissolution of calcite and if it is greater than 2 indicates the weathering of silicate mineral and ion exchange. From the collected water samples 13.33 %, 48.33 % and 38.33 % of water samples have less than one, between one and two and greater than two respectively (Figure 19a).

The molar ratio of Na^+/Cl^- is also used as an indicator to identify the geochemical process that controls groundwater chemistry. Greater than one value of the ratio of Na^+/Cl^- indicates silicate weathering or ion exchange. On the other hand, if the ratio of Na^+/Cl^- is near to one, this is an indicator that the source of Na and Cl^- is halite dissolution (Numanbakth et al., 2019; Sheikhy Narany et al., 2014; Yang et al., 2016).

In the study area, Zamra catchment 83.33 % and 16.67 % of the water samples have greater than one and less than one molar ratio of Na^+/Cl^- respectively (Figure 19b). In Zamra catchment there is not an indication of halite dissolution.

To identify the dominant geochemical processes whether silicate weathering or ion exchange, the relationship between (Ca +Mg) -(SO4 + HCO3) and (Na -Cl) is used a reference. If the geochemical process is dominated by ion-exchange the regression line between (Ca +Mg) -(SO4 + HCO3) and (Na-Cl) shows a negative relationship and it is positive if silicate weathering is dominance (Aghazadeh et al., 2017; Sheikhy Narany et al., 2014). The result from the study area, Zamra catchment shows that there is a positive correlation between (Ca +Mg) -(SO4 + HCO3) and (Na-Cl) which indicates a dominance of silicate weathering (Figure 19c).

The high concentration of (SO4 + HCO3) relative to (Ca +Mg) is an indicator for silicate weathering than the dissolution of calcite, dolomite and gypsum (Aghazadeh et al., 2017). There is a dominance of sulfate and bicarbonate than the calcium and magnesium cations in the study area and this is an indicator for dominance of silicate weathering (Figure 19d). The correlation of $SO4^{2-}$ with Ca^{2+} and Mg^{2+} is very low (R^2 =0.0725). This is also a good indicator that they have no same source with sulfate and further indicates the dominance of silicate weathering than a dissolution of calcite and dolomite.

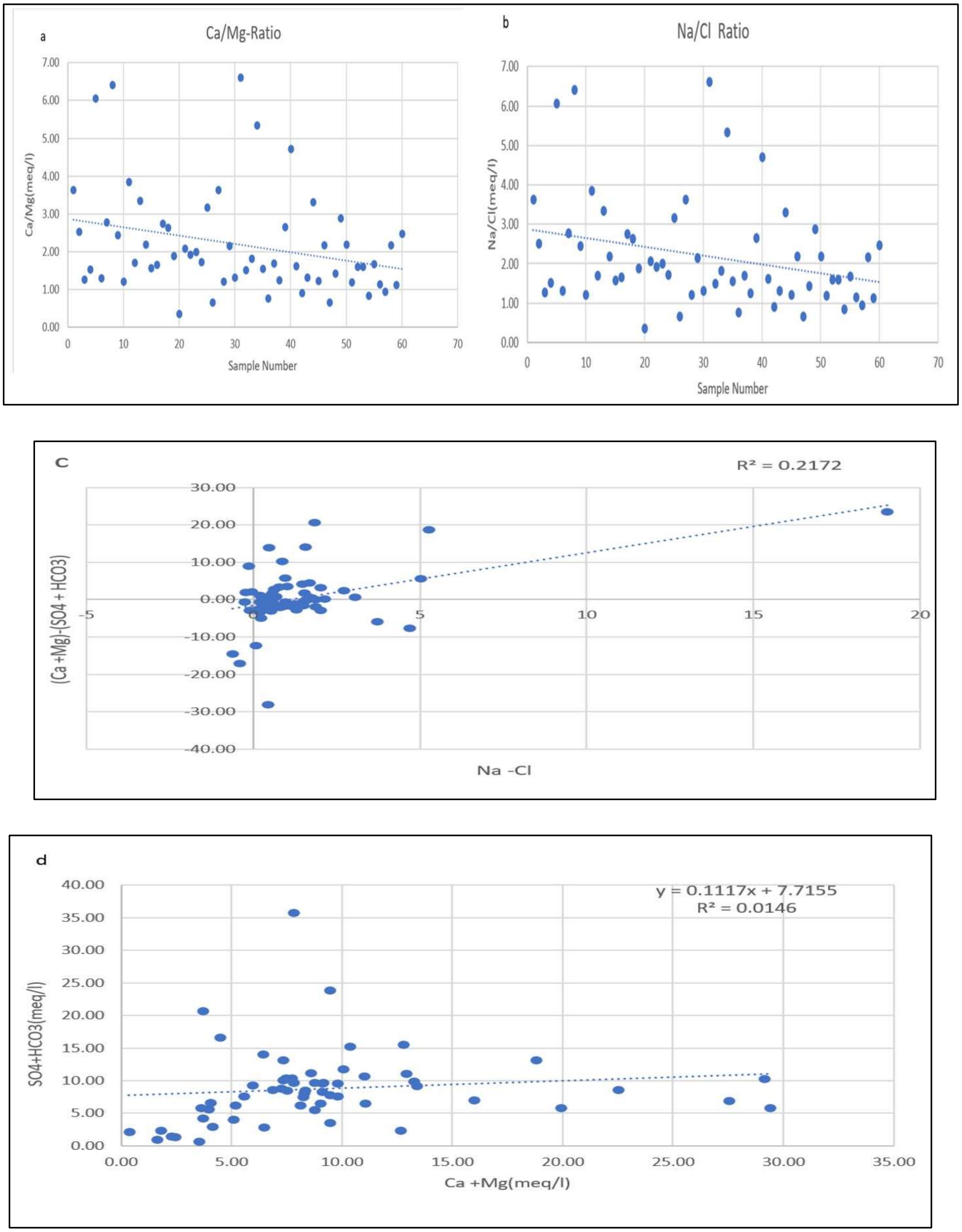


Figure 19: Distribution of ionic ratios (a) Ca^{2+}/Mg^{2+} ratio, (b) Na/Cl ratio, (C) plot of Ca +Mg) -(SO4 + HCO3) VS (Na -Cl) and (d) plot of (SO4 + HCO3) VS (Ca +Mg) ions.

The geochemical processes that control the water chemistry in the study area are silicate weathering, dissolution of dolomite and precipitation of calcite.

Spatially there is significant variation in TDS and EC in the study area, with the variations in the range between 72.8 to 3276 mg/l and 112 µs/cm to 5040 µs/cm. This is an indicator that there is an anthropogenic activity that such as fertilizers and landfills that can cause deterioration in water quality (Sheikhy Narany et al., 2014).

Positive Correlation of TDS with $(NO3^{-} + Cl^{-})/Na^{+}$ and $(NO3^{-} + Cl^{-})/HCO3^{-}$ implies impact anthropogenic activity on water quality (Marghade, Malpe, & Zade, 2011). In Zamra catchment the correlation between TDS with $(NO3^{-} + Cl^{-})/Na^{+}$ and $(NO3^{-} + Cl^{-})/HCO3^{-}$ is R^2=0.0172 and R^2=0.1998, respectively. The correlation is positive which implies anthropogenic impact on water quality.

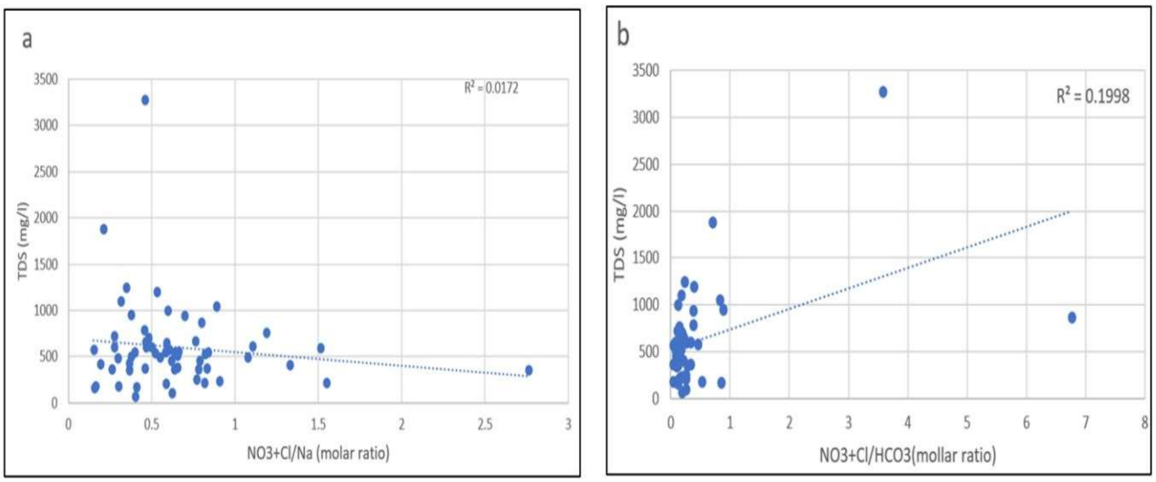


Figure 20: Correlation of TDS with (a) (NO3- + Cl-)/Na+, (b) with (NO3- + Cl-)/HCO3-

5.5 Hydrogeochemical modeling Using NETPATH

Saturation index is an indicator used to determine the state of equilibrium of water with respect to the mineral phase. Saturation index is determined using the hydrogeochemical model, NETPATH. The result is presented in Appendix VI.

The result from NETPATH model indicates that precipitation of calcite, aragonite, dolomite, siderite, rhodochrosite, gypsum, barite, goethite, Pyrolusite and hematite and dissolution of anhydrite, witherite, Fe (OH)3, Manganite, pyrochrosite, hausmanite and K-Jarosite controls the grounwater chemistry in the study area. These are minerals of carbonate, sulfate, iron, manganese, and clay(silicate). In addition to this dissolution of gypsum and anhydrite also occurs in the lower Zamra catchment.

Saturation of mineral is different spatially with mainly with geology. Dolomite has lower degree of saturation in basalt relative to other rock types. SI is low in surface water than groundwater Appendix VI. This is an indicator in groundwater there is relatively high water-rock interaction because its stagnant and groundwater flows at very low-speed relative to surface water.

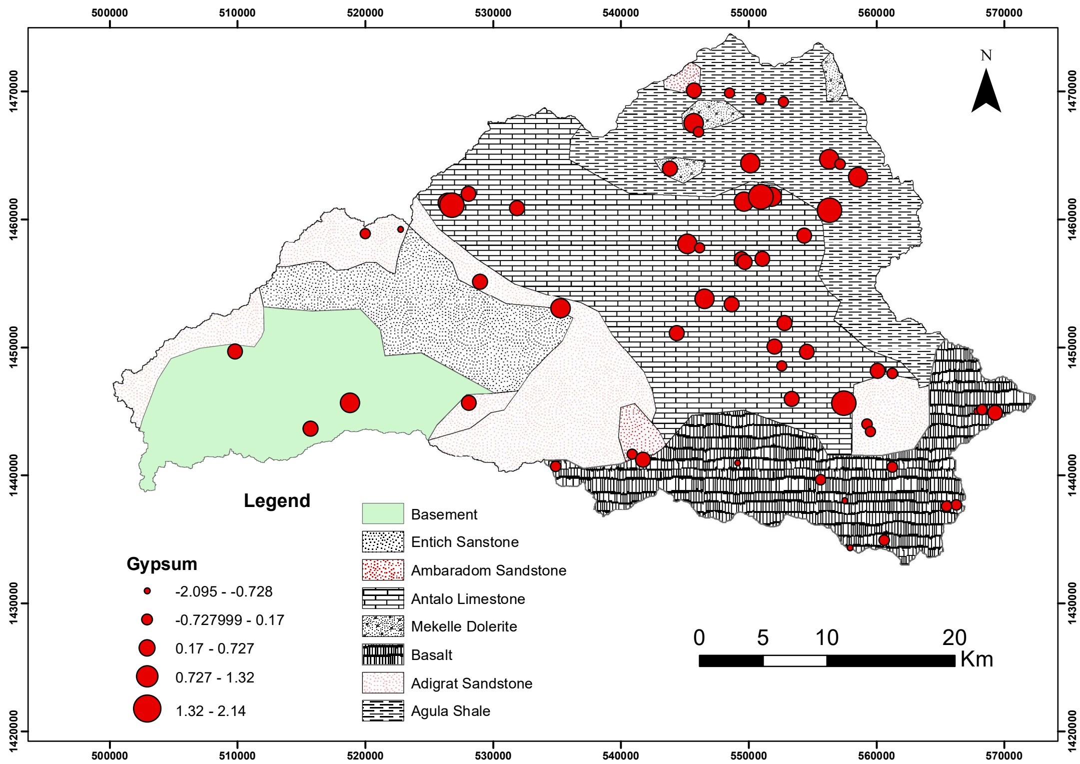


Figure 21: Spatial distribution of Gypsum in relation to different geological formations

5.6 Relationship of Water quality parameters with Geology and LULC

Originally the water from precipitation is diluted and has low chemical constituents. To reach the groundwater, water passes through the porous and unsaturated zones. A chemical reaction occurs when water passes through unsaturated zones due to the water-rock interaction and this changes chemistry of water from precipitation (Sheikhy Narany et al., 2014). The concentration of the major cations and anions are used to determine the impact of geology and LULC on water quality parameters.

To determine the relationship between WQ parameters and geology statistical mean of water samples collected only groundwater samples are considered because surface waters are affected by anthropogenic factors.

Ca^{2+}, $SO4^{2-}$, and total hardness have high concentrations high in Antalo limestone. This implies the hardness in limestone will be most probably due to the high concentration of calcium.

Na^{+} and Cl^{-} are found in high concentration in Agulae shale. Magnesium, bicarbonate, EC and TDS and alkalinity are found in high concentration in the basement rock. This infers rock is originally from volcanic rock which is called meta-volcanic.

The abundance of the elemental concentrations and the physicochemical parameter is different in relation to different geological formations this helps to know the geochemical process that can change groundwater chemistry.

In relation to LULC, the result indicates that NH3 and P are found abundantly in agricultural land than the other land uses. This is an indicator there is an impact of fertilizers and pesticides. Cl, EC, and TDS are having high concentrations in bare land. In the LULC map, the small cities are mapped as bare land and there was waste disposal around Hiwane city, and this can be a reason for the high concentration of these WQ parameters. And the area very rugged can also result in miss classification and agriculture can also be classified as bare land. The relative abundance of elements relative to LULC is presented in Table 7.

The result indicates all the major cations and anions, EC, TDS, and alkalinity have high concentrations in basement rock except sulfate, TH, chloride, and PH which are observed in high concentrations in Antalo limestone, Ambaradom sandstone, Mekelle dolerite, and basalt respectively.

Basement rock is exposed in the downstream part of the study area and the water flows from upper catchment t the lower catchment with many paths through porous of different rock types. During the flowing it water interacts with rocks and this can change the constituents of WQ parameters as it flows long paths. The other reason can is basement rock is the oldest rock compared to the other rock types found in the study area and water can be in interaction with the rock for a long time. This can be a reason to have a high concentration of the WQ parameters in the basement rock.

The result of descriptive statistics indicates different geological formations and LULC affects differently for different WQ parameters. The parameters used to visualize maps in relation to are selected by their high spatial variations with geology. The parameters affected by LULC are used to visualize the spatial distribution of WQ in different LU types (Figure 22).

Table 7: Relative abundance of selected WQ parameters in relation to geology and (b)LULC

Geology	HCO3 (mg/l)	Geology	Mg (mg/l)	Geology	EC (mg/l)
Basement	587.7875	Basement	87.99	Basement	1462.3
Basalt	395.9937	Agulae shale	49.13	Agulae shale	1365
Agulae shale	386.2313	Adigrat Sst	35.53	Antalo Lst	1080
Antalo Lst	379.1709	Basalt	33.4442	Adigrat Sst	720.45
Amba Aradom Sst	366.096	Antalo Lst	32.4308	Basalt	641
Adigrat Sst	347.7912	Amba Aradom Sst	28.208696	Amba Aradom Sst	574

Geology	TH (mg/l)	Geology	Cl (mg/l)	Geology	Alkalinity (mg/l)
Antalo Lst	497.14	Agulae shale	110	Basement	963.3
Agulae shale	483	Basement	92.67	Basalt	685
Basement	470	Antalo Lst	41.71	Agulae shale	633
Adigrat Sst	312.5	Adigrat Sst	36.5	Antalo Lst	621.43
Basalt	267	Basalt	25.8	Amba Aradom Sst	600
Amba Aradom Sst	260	Amba Aradom Sst	15	Adigrat Sst	570

Geology	Ca (mg/l)	Geology	SO4 (mg/l)	Geology	TDS (mg/l)
Antalo Lst	183.5411	Antalo Lst	240	Basement	950.51667
Agulae shale	165.4275	Basement	220	Agulae shale	887.25
Basement	135.33	Agulae shale	170.4	Antalo Lst	702.18571
Adigrat Sst	98.624	Adigrat Sst	44	Adigrat Sst	468.2925
Basalt	61.2444	Basalt	33.3	Basalt	416.65
Amba Aradom Sst	34.51	Amba Aradom Sst	19	Amba Aradom Sst	373.1

Geology	Na (mg/l)	Geology	K (mg/l)	Geology	PH
Agulae shale	135.4416	Amba Aradom Sst	0.388	Basement	7.841
Basement	126.0983	Basalt	0.8938	Agulae shale	7.62
Antalo Lst	53.53871	Antalo Lst	2.352	Antalo Lst	7.379
Basalt	50.0238	Agulae shale	2.4069	Adigrat Sst	7.373
Adigrat Sst	41.3175	Adigrat Sst	5.763	Basalt	7.28
Amba Aradom Sst	11.865	Basement	10.88	7.2525	Amba Aradom Sst

LULC	EC	LULC	TDS	LULC	NH3
Bare land	1611.76	Bare land	1047.64	Agriculture	0.12
Forest	1093.22	Forest	710.59	Water	0.12
Agriculture	805.33	Agriculture	523.47	Bare land	0.11
Water	314.5	Water	204.43	Forest	0.11

LULC	PH	LULC	Cl	LULC	P
Water	9.35	Bare land	168.80	Agriculture	0.11
Agriculture	7.70	Forest	50.33	Water	0.07
Forest	7.56	Agriculture	35.58	Bare land	0.06
Bare land	7.54	Water	18.25	Forest	0.05

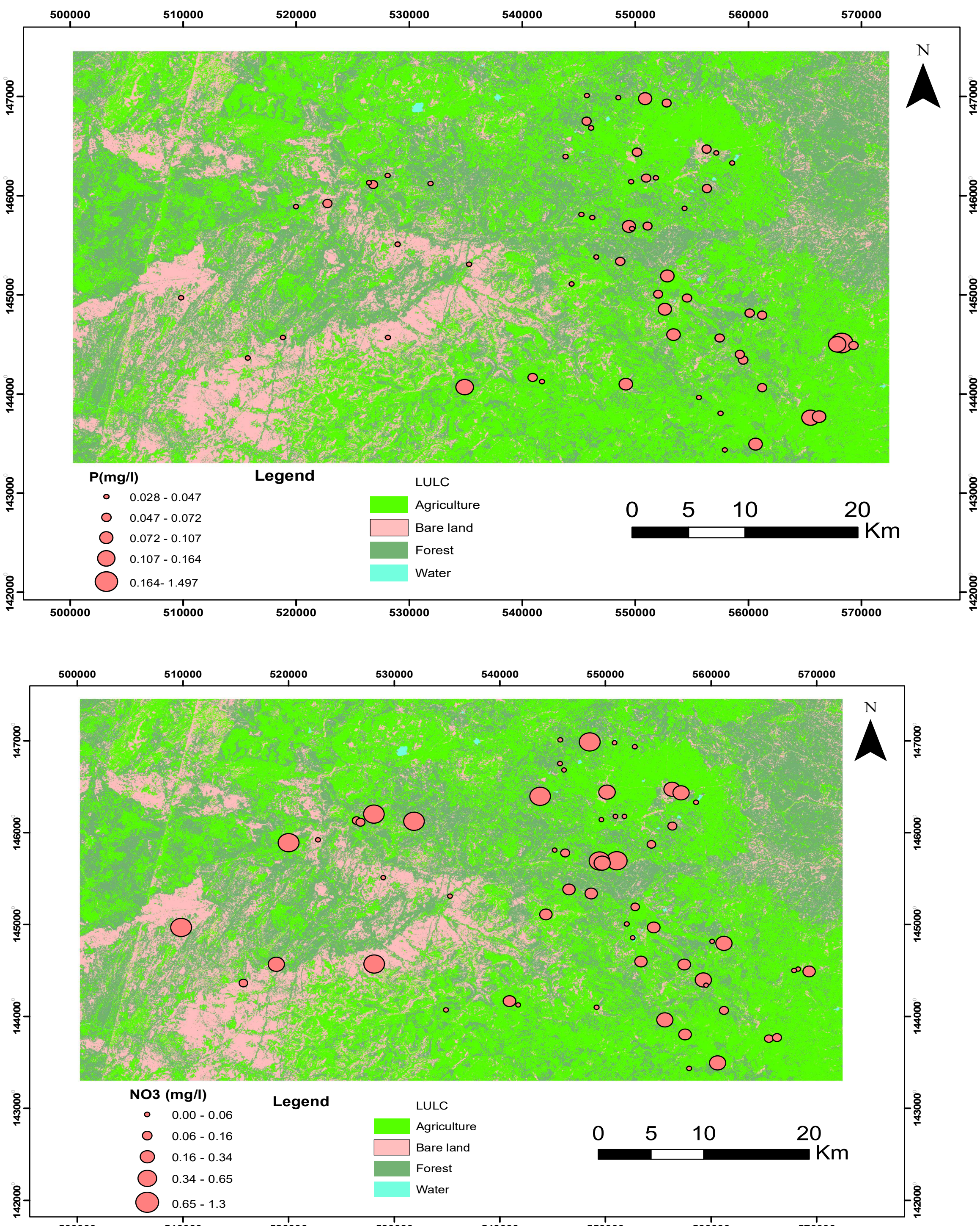
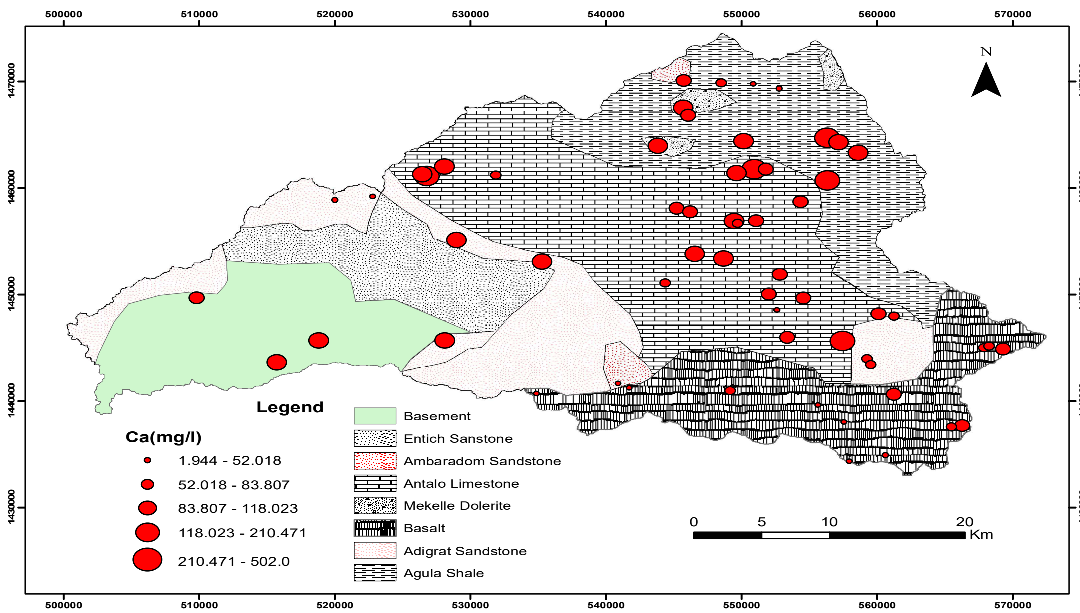
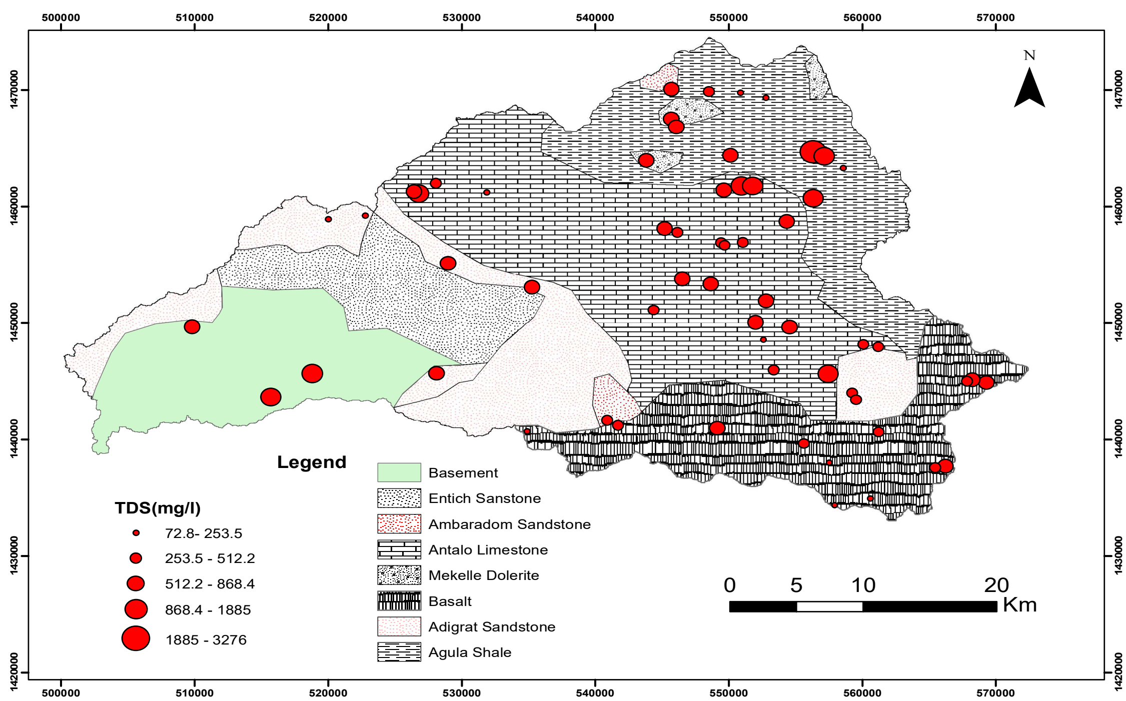


Figure 22: Spatial of distribution of P and NO3- in relation to LULC


Legend
Ca(mg/l)
1.944 - 52.018
52.018 - 83.807
83.807 - 118.023
118.023 - 210.471
210.471 - 502.0
Basement
Entich Sanstone
Ambaradom Sandstone
Antalo Limestone
Mekelle Dolerite
Basalt
Adigrat Sandstone
Agula Shale
0 5 10 20 Km
N


Legend
TDS(mg/l)
72.8- 253.5
253.5 - 512.2
512.2 - 868.4
868.4 - 1885
1885 - 3276
Basement
Entich Sanstone
Ambaradom Sandstone
Antalo Limestone
Mekelle Dolerite
Basalt
Adigrat Sandstone
Agula Shale
0 5 10 20 Km
N

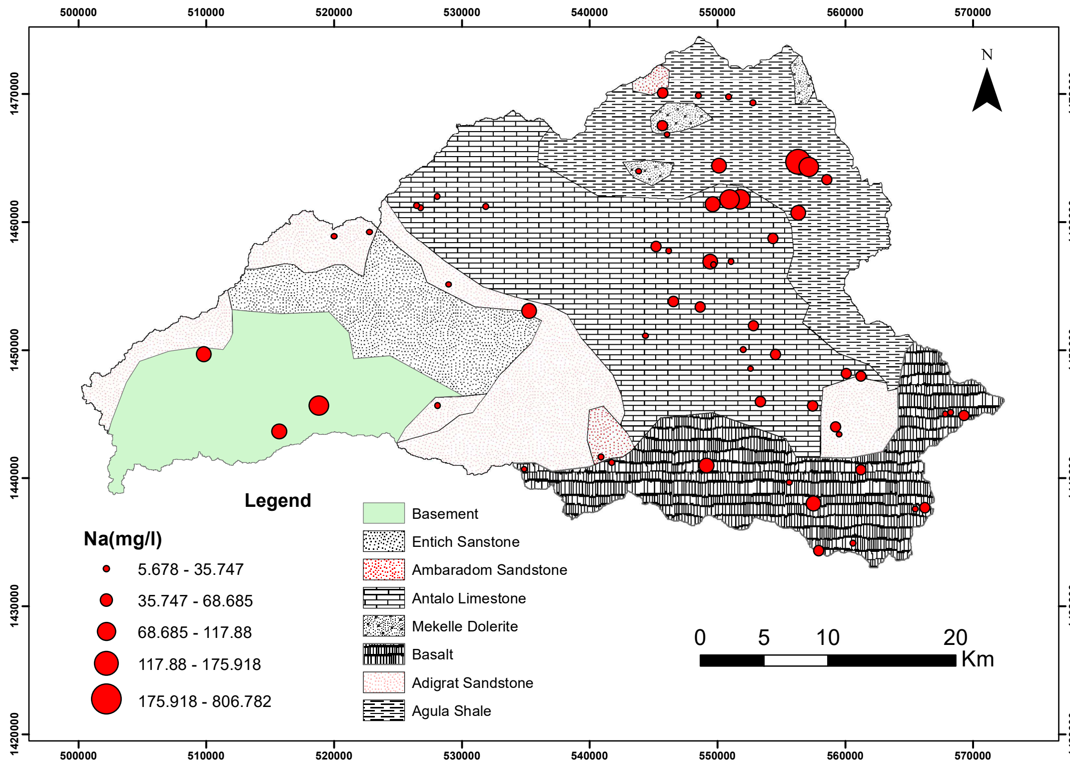


Figure 23: Spatial of distribution of Ca, Na and TDS in relation to geology

5.7 Water quality Assessment and Evaluation

The suitability is evaluated for irrigation and drinking by comparing the chemical constituents of the water samples with the national and international standards such as Ethiopian standards, WHO and FAO standards (Compulsory Ethiopian Standard, 2013; FAO, 1985; WHO, 2008; Wilcox, 1955).

5.7.1 Suitability of Water for Irrigation Purpose

"Irrigation water quality refers to the kind and concentration of the available elements present in the water used for irrigation and their effect on crop growth and production" (Kahsay et al., 2019, p. 80) . The most important parameters to evaluate the suitability of water for irrigation are SAR or sodium hazard, Salinity hazard, PI, Kelly's ratio and MAR (FAO, 1985; Kahsay et al., 2019; Wilcox, 1955).

Salinity

The salinity of water is related to EC and TDS of the water samples. According to (FAO, 1985) EC and TDS up to 3000 µs/cm and 2000 mg/l is possible to use for irrigation purposes respectively. SHW19 has 5040 µs/cm of EC and 3276 mg/l of TDS and this is beyond the permissible limit.

Sodium Adsorption Ratio (SAR)

SAR is the ratio of sodium to calcium and magnesium ions in meq/l. The concentration of SAR in Zamra catchment ranges from 0.18 to 9.13 meq/l. Compared to (FAO, 1985) classification except SHW19 all water samples are suitable for irrigation purpose.

EC and SAR of the water samples are also evaluated using the Wilcox classification method. According to the(Wilcox, 1955), there are four-class water in Zamra catchment. All water samples fall in the S1 class which is low alkali hazard except SHW19. Based on EC, the water samples fall into four classes (Figure 24). The water samples fall in C3 and C4 are not recommended to use for irrigation purposes in a normal conditions that means it needs spatial management for salinity control (Wilcox, 1955). The C3 and C4 water classes are indicated high salinity hazard. Surface water sample collected from OPW1, SP7, OPW3, RV3, CD1, CN5, SP2, SP4, SP9, SP3, CN6 and groundwater samples collected from HDW1, SHW1, SHW6, DW2, DW3, HDW4, HDW5, SHW7, HDW6, SHW9, HDW7, HDW8, SHW10, SHW12, SHW13, SHW14, SHW15, SHW16, SHW17, SHW18, HDW10, SHW19, HDW11, DW4 are grouped in C3, high salinity class and SP8 is grouped in C4, very high salinity class.

Kelly's Ratio (KR)

93.3 % of the water samples have less than one KR and they are suitable for irrigation purposes. 6.67 % of the water samples collected (SHW2, DW1, SHW19 and SHW10) have greater than 1 KR values and are classified under unsuitable class. SHW2 has highest KR. This is because of the dominance of Na ions compared to Ca and Mg. Bothe SHW2 and DW1 are sampled from Basalt exposure and SHW10 is sampled from Antalo limestone.

Permeability Index (PI)

There are two classes of water in Zamra catchment based on PI. Class II with PI between 25 to 75 % and this covers far the 93.5 % of the water samples. Water samples collected from CD1, DW3, SHW18 and SP8 have PI less than 25 % which is unsuitable for irrigation purposes. CD1 and SHW18 are collected from the upstream of Zamra river (RV3).

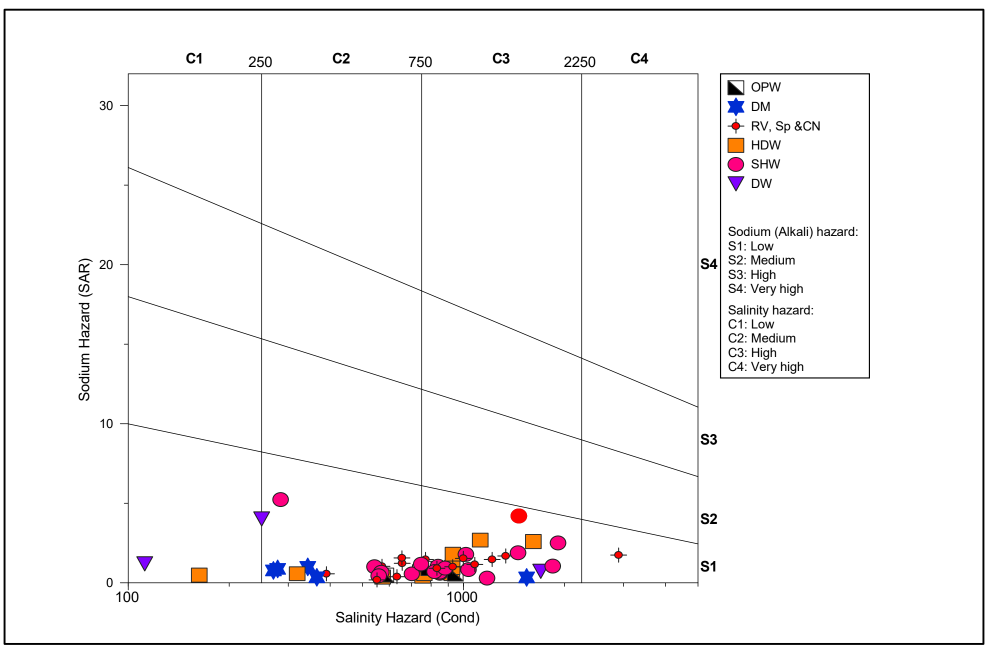


Figure 24: Water quality classification for irrigation use, Wilcox plot

Magnesium Adsorption Ratio (MAR)

MAR in the study area ranges from 8.95 to 94.09 %. Based on this parameter DW1 is classified in the unsuitable water for irrigation purpose. This is an indicator for high Mg ion relative to calcium ion. High Ma results in alkaline water and the harms crop yield productivity.

Anions and Cations

The availability of cations and anions is important for plant growth. According to (FAO, 1985), the permissible ranges of irrigation water for the cations is 0-20 meq/l (for Ca), 0-5 meq/l(for Mg), 0-40 meq/l (for Na), 0-2 meq/l (for K). All the water samples in the study area have sodium and potassium concentrations in the range of the permissible limit. SP8 and DW3 have calcium concentration above the permissible limit. SHW12, SHW14, SHW15, SHW19, HDW11, RV3, SHW18, CD1 have Mg ion above the permissible limit.

Based on (FAO, 1985), the permissible limit for anions is 0 to 10 meq/l for bicarbonate, 0 to 30 for chloride, 0 to 20 for sulfate. The water samples are permissible for irrigation purpose with respect to anions except SP8 and SHW19 which have beyond the permissible limit of $SO4^{2-}$ and Cl^{-}, respectively. A higher concentration of chloride in irrigation water is toxic to plants and crops (Wilcox, 1955).

Poor water quality can cause to destruction of soil structure, damage irrigation equipment's due to corrosion and encrustation, and it result in failure of crop production.

70 % of the groundwater samples from the study area have high to very high salinity hazed. Most of high saline groundwater samples are collected from Agulae shale and Antalo limestone.

The high salinity ca affects for the crops and trees sowed in the study area such as stone-fruit trees and avocados that are highly sensitive to sodium.

To reduce the effect of salinity on crop production, high salinity resistance crops like Barley, cauliflower, cotton, sorghum and sunflower are recommended to be sowed in the study area, Zamra catchment. And leaching is also powerful solution (FAO, 1985) to reduce salinity hazard. This means high water is required to during the irrigation period to percolate the accumulated salt at the root of crops.

5.7.2 Suitability of Wate for Drinking Purpose

The water samples are evaluated their suitability for drinking purposes by comparing their chemical constituents with international (WHO, 2008) and national (Compulsory Ethiopian Standard, 2013) standards. The evaluation for drinking purpose is conducted for the water samples which are collected from water points used for household use and agriculture. Water samples collected from dam, river, canal, and open well are not included in this evaluation be because they are used only for irrigation purpose.

Physicochemical parameters

The PH in the study ranges from 6.83 to 9.61. According to Ethiopian and WHO standards PH between 6.5 to 8.5 is permissible for drinking purposes. DW1 and SHW1 have a PH 9.61 and 9.57 receptivity which is above the permissible limit. All these are collected from Basalt rock exposure.

According to (WHO, 2008) less than 750 µs/cm EC is permissible for drinking purpose. Water samples collected from HDW1, SHW1, SHW6, SP4, SP3, DW2, DW3, HDW4, HDW5, SHW7, HDW6, SHW9,

HDW7, HDW8, SP7, SHW15, SHW16, SHW12, SHW10, SHW13, SHW14, SHW17, SHW18, HDW10, SHW19 and HDW11 have EC greater than 750 µs/cm. The maximum EC, 5040 µs/cm is recorded in SHW19 which is collected from a shallow well to Adigudem city.

TDS less than 1000 mg/l is suitable for drinking purpose. There are two types of water classes in Zamra catchment based on TDS, fresh (TDS less than 1000mg/l) and brackish (TDS greater than 1000mg/l). SHW6, DW3, SHW15, SHW19, HDW11 have TDS above 1000 mg/l and are undesirable for drinking purpose.

The total hardness found the range of 250 to 920 mg/l. According to the Ethiopian standard water with TH less than 300 mg/l is desirable for drinking purpose and TH up to 500 is suitable for drinking purposes based on the WHO standard. SHW1 and SHW14 have below the permissible limit of the Ethiopian standard. SHW3, DW3, SHW15, SHW18, SHW19 and HDW 11 have TH above the standard stated by WHO. Using of water with high TDS and TH can cause gastrointestinal irritation and disease of kidney, respectively.

Cation and Anion Concentrations

Calcium ion: Compared to (WHO, 2008) and (Compulsory Ethiopian Standard, 2013) standards except HDW1 and SP7 all water samples are not suitable for drinking purposes. 72 mg/l of calcium is the maximum permissible limit in drinking water. The higher concentration of calcium ion can cause failure of a kidney (Kahsay et al., 2019) and this is common problem in the study area, even in whole country, Ethiopia.

Sodium ion: Except for SHW19 that has 806.782 mg/l of Na ion, all water samples are permissible to use for drinking purposes. This can cause hypertension, circulatory disease and kidney problems (Kahsay et al., 2019; Sakram & Adimalla, 2018).

Magnesium ion: There are different permissible standards for concentration magnesium in the drinking water from the Ethiopian standard and WHO, 50 mg/l and 30 mg/l, respectively.

7 water samples collected from SP2, SHW12, SHW14, SHW15, SHW18, SHW19, and HDW11 are found with Mg having above the permissible limit. Higher magnesium concentration in drinking water results in a laxative effect for a human being.

Potassium ion: According to the Ethiopian Standard, the maximum allowable concentration of potassium in drinking purpose is 1.5 mg/l. Water samples collected from HDW1, SHW1, SP2, SP4, DW3, HDW5, HDW6, SHW10, SHW13, SHW14, SHW15, SHW16, SHW17, SHW18, SHW19, HDW have potassium ion above the permissible limit. Higher potassium in drinking water results in hypertension and high blood pressure (Kahsay et al., 2019).

Anions such as chloride and sulfate are recorded above 250 mg/l, desirable limit in SHW19 and SHW6, DW3, SHW10 and SHW15, respectively.

All the water samples have concentrations of Zn, Mn, Cu, Ba, Se, Cr, NH3 and $NO3^-$ ions of below the permissible limit. The concentration of toxic elements such as As (in all water samples), Cd (in HDW 11 and SHW1) and Pb (in HDW1, SHW1 and SHW6, B in SHW19) are found beyond the permissible limit stated by WHO and the Ethiopian standards.

The health problems raised because water quality problems which are published by different scholars are common in the study area, Tigray. Then treatment is required for the water points that are found above the permissible limit.

The List of location such as longitude, latitude and their specific Woreda, Tabia and site name of water samples and the specific water quality problem in drinking and irrigation purpose will be submitted to ENSSAT project for further investigations and to deal in contact with the local experts.

Treatment of Drinking water: The water samples that have a higher concentration of anions, cations, and toxic elements are recommended for treatment. Especially water sample collected from SHW19 shows extreme values in most of the WQ parameters. The treatment methods such as chlorination (for chloride and As), chemical coagulation (for surface water), and ion exchange (for As, hardness) methods can be used for the removal of the elements that are found beyond the permissible limit in Zamra catchment. These treatment methods for selective elements are provided by (WHO, 2008).

SHW19 which is used for drinking purposes needs special attention because it does not fitful even to use for irrigation purposes. It is characterized by poor water quality based on all the parameters used to evaluate for irrigation as wells as for drinking purposes.

6 CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The study is conducted in Zamra catchment, Tigray, northern Ethiopia. Irrigation is the main source of the economy in the study area. 60 water samples were collected for physicochemical analysis. The physiochemical parameters such as PH, EC, TDS. alkalinity, chloride, TH were analyzed in the field parallel to field data collection whereas cation and anion were analyzed in the ITC Geoscience laboratory.

Aquachem, NETPATH model and statistical methods were used to identify water types and the geochemical processes that control the groundwater chemistry.

Chemistry of groundwater shows a spatial variation with geology, elevation, scheme type, and LULC. It is dependent on all these elements.

The dominant major ions are HCO3> SO4> Ca > Na >Mg >K, respectively. The study area is dominated by magnesium bicarbonate water type specifically Na-Mg-Ca-HCO3, Ca-HCO3-SO4 followed by chloride water types. The chloride water type is observed only in SHW19.

The geochemical processes that control the groundwater chemistry in the study area are silicate weathering, precipitation of calcite, and dissolution of dolomite. There is also the impact of the anthropogenic activity that deteriorates water quality. SI determined using NETPATH indicates the oversaturation of carbonate minerals.

70 % of the groundwater samples are characterized by high to very high salinity hazard. SHW19 has extreme salinity and its quality fails compared to most WQ standards used to evaluate drinking and irrigation water quality.

The water quality is also evaluated for drinking purposes. Most of the water samples have above the desirable limit of EC, TDS, TH, Ca and As. SHW19 is found unsuitable with almost all parameters. Na is found within the permissible limit except in SHW19.

A descriptive statistic is used to determine the relationship between WQ parameters with geological formations and LULC types. The result indicates that there the Sulfate, Ca and TH have high concentration in Antalo limestone whereas Mg has a higher concentration in the basement (meta-volcanic).

Recommendations

- The water samples are collected from different water points which are mainly selected by the secondary data such as lithological data, geological map, few water quality, and distribution of water points collected from different offices. Unfortunately, in some parts of the study area, geology was not as expected, and because of this, there was no sample collected from Enticho sandstone. In case, for the next, if sampling of water from the study area is required, it is recommended to cross-check the geology of the sampling point by making traverse before starting sampling.
- The geology in the study area is complex and it needs detailed investigation and traversing to have an accurate geological map that represents the study area, Zamra catchment.

- The anions except for Cl^-, $HCO3^-$ and $CO3^{2-}$ were analyzed after a long time of keeping the water samples in the refrigerator and this can be caused to lose the concentration of anions. To have a full interpretation of the water quality of the area I recommend analyzing the anions for further study, especially the water points because of the quality problem that needs treatment.
- Salinity hazard is found high to very high in the study area. Leaching is recommended to minimize the concentration of salt. Beyond this to determine the leaching time and amount of water required for leaching detailed information on the depth water table and soil property. These two parameters should be studied in detail to have proper irrigation water management in Zamra catchment.
- SHW19 is classified in the unsuitable class compared to most of the WQ parameters. SHW19 needs special attention and treatment because this found near the small city called Adigudem and this is used for drinking purposes. Chlorination, chemical coagulation, and ion exchange will help for the remediation of the water chemistry which is undesirable for drinking purposes.

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APPENDICES

Appendix I: Water Quality data collected from Secondary data

No	Sample Code	X	Y	Z	Geology	Parameters				
						EC (µs/cm)	PH	Temp	Li(mg/l)	Na(mg/l)
1	BH20	554086	1450963	2002	Shale, Marl, Lst	1576	7.5	24	0	47
2	DW11	556473	1461799	2092	Lst, Shale, marl	1076	7.7	21	0	85.2
3	R10	538590	1445740	1695	Lst, Dolerite	567	8.8	25	0	25
4	SP17	539168	1457006	1955	Lst, Dolerite	1200	8.5	21	0	65
5	SP24	527613	1461672	2156	Lst, Dolerite	297	8.2	15	0	12.8
6	SP15	558283	1444110	2116	Sandstone, basalt	530	7.7	30	0	15.8
7	SP14	558921	1435750	2703	Basalt	849	7.2	24	0	38.9
8	R9	555450	1440599	2516	Basalt, Sst	1577	7.3	23	0	21.9
9	DW1	559241	1464914	2052	Shale	3037.85	7.02	22	0	82
10	SHW3	39.177	13.201	1925	Adigrat Sst	593	7.9	20	0	34
11	SHW5	39.146	13.199	1989	Adigrat Sst	1028	7.9	19	0	75
12	BH-190	39.069	13.097	1497	Basement	753	6.72	24	0	14

No	Sample Code	Parameters							
		k(mg/l)	Mg(mg/l)	Ca (mg/l)	HCO3 (mg/l)	SO4- (mg/l)	NO3- (mg/l)	Cl- (mg/l)	F-(mg/l)
1	BH20	2.4	61	287	372.22	870	4	27	0.7
2	DW11	2.2	42	85.5	384.43	283	1.4	43	1.3
3	R10	1.4	28	54.6	484.43	34	10.7	12.1	0.5
4	SP17	2.6	56	146	317.3	500	4	53.4	4.1
5	SP24	0.3	11	45	213.57	7.5	3	4	0.3
6	SP15	0.8	19	79.9	378.32	16.7	11.8	8.9	0.4
7	SP14	0.9	24	126	433.24	72.8	56.7	32	0.7
8	R9	1.5	57	319	439.34	817	0	14	1
9	DW1	1.03	15	205	20	21	17	13	0.004
10	SHW3	1.01	19	102	199.7	139.7	0.09	31.54	0.003
11	SHW5	1.03	31	104	231.7	345	0.11	41.56	0.006
12	BH-190	1.08	14	113	241.54	131.78	0.06	8.87	0.003

Appendix II: Physicochemical parameters measured in the field, Zamra Catchment

No	X	Y	Code	PH	EC (µs/cm)	Chloride (mg/l)	TDS (mg/l)	TH (mg/l)	Color	Odor
1	549145	1440977	HDW1	7.78	1121	50	728.65	350	Colorless	Odorless
2	566257	1437706	SHW1	7.09	840	30	546	250	Colorless	Odorless
3	565482	1437583	RV1	8.08	704	38	457.6	300	Colorless	Odorless
4	553373	1445970	OPW1	7.35	788	45	512.2	350	Green	Odorless
5	557934	1434352	SHW2	9.61	285	13	185.25	80	Colorless	Odorless
6	560618	1434932	CN1	8.55	390	22	253.5	230	Colorless	Odorless
7	555627	1439640	SHW3	7.59	543	18	352.95	250	Colorless	Odorless
8	557540	1438034	DW1	9.57	250	20	162.5	50	Colorless	Odorless
9	552592	1448532	DM1	9.2	271	15	176.15	140	Colorless	Odorless
10	540899	1441649	HDW2	7.62	574	15	373.1	260	Colorless	Odorless
11	541729	1441233	SHW4	7.69	569	10	369.85	200	Colorless	Odorless
12	534884	1440698	HDW3	6.83	319	16	207.35	180	Colorless	Odorless
13	561239	1440643	SHW5	7.26	747	25	485.55	400	Colorless	Odorless
14	559252	1443986	CN2	8.77	571	30	371.15	240	Colorless	Odorless
15	559539	1443412	CN3	8.73	557	32	362.05	250	Colorless	Odorless
16	554567	1449664	CN4	8.53	894	50	581.1	420	Colorless	Odorless
17	561231	1447954	RV2	8.32	656	30	426.4	300	Colorless	Odorless
18	560101	1448169	CN5	8.09	770	40	500.5	350	Colorless	Odorless
19	556335	1460714	SHW6	7.22	1846	62	1199.9	550	Colorless	Odorless
20	544375	1451105	SP1	7.38	552	24	358.8	250	Colorless	Odorless
21	546545	1453810	SP2	7.06	1080	50	702	470	Colorless	Odorless
22	552819	1451907	SP4	7.37	833	36	541.45	450	Colorless	Odorless
23	548666	1453370	SP3	7.22	928	40	603.2	520	Colorless	Odorless
24	552015	1450056	DW2	7.35	844	32	548.6	370	Colorless	Odorless
25	557447	1445636	DW3	7.44	1699	30	1104.35	920	Colorless	Odorless
26	543829	1463957	HDW4	7.2	922	66	599.3	450	Colorless	Odorless
27	545694	1467525	HDW5	7.34	925	20	601.25	420	Colorless	Odorless
28	546074	1466830	SHW7	7.32	820	40	533	390	Colorless	Odorless
29	550144	1464388	HDW6	7.34	929	62	603.85	350	Colorless	Odorless
30	548503	1469876	SHW8	7.29	559	20	363.35	300	Colorless	Odorless
31	545721	1470091	SHW9	7.37	882	10	573.3	480	Colorless	Odorless
32	545211	1458108	HDW7	7.34	861	40	559.65	350	Colorless	Odorless
33	546187	1457780	HDW8	7.26	764	22	496.6	410	Colorless	Odorless
34	549452	1456895	SP5	7.36	655	22	425.75	320	Colorless	Odorless
35	549712	1456677	OPW2	7.52	586	18	380.9	260	Green	Odorless
36	551075	1456920	SP6	7.48	633	36	411.45	300	Colorless	Odorless
37	554354	1458728	SP7	7.73	998	62	648.7	420	Colorless	Odorless
38	549633	1461411	CN6	9.01	1336	120	868.4	520	Colorless	Odorless
39	551802	1461784	SHW10	7.98	1463	100	950.95	350	Colorless	Odorless
40	550942	1461774	SP8	7.63	2900	50	1885	1350	Colorless	Odorless
41	567859	1445001	SHW11	7.57	701	24	455.65	410	Colorless	Odorless
42	568246	1445148	OPW3	8.34	945	42	614.25	420	green	Odorless

43	569302	1444883	SHW12	7.42	1035	52	672.75	500	Colorless	Odorless
44	552734	1469199	DM2	9.74	279	10	181.35	110	Colorless	Odorless
45	550962	1469423	DM3	10.4	343	32	222.95	100	Colorless	Odorless
46	509813	1449679	SHW13	7.7	1017	64	661.05	390	Colorless	Odorless
47	519994	1458897	SP9	6.88	330	28	214.5	240	Colorless	Odorless
48	515717	1443633	SHW14	7.11	1455	120	945.75	270	Colorless	Odorless
49	518805	1445674	SHW15	7.03	1915	94	1244.75	750	Colorless	Odorless
50	535286	1453076	RV3	8	1217	60	791.05	560	Colorless	Odorless
51	528974	1455113	SHW16	7.31	851	40	553.15	410	Colorless	Odorless
52	528103	1445684	SHW17	7.17	851	32	553.15	380	Colorless	Odorless
53	522779	1459209	HDW9	6.83	162.8	10	105.82	70	Colorless	Odorless
54	526446	1461291	SHW18	7.05	1176	34	764.4	670	Colorless	Odorless
55	526792	1461121	CD1	7.77	1542	24	1002.3	850	Colorless	Odorless
56	531866	1460894	DM4	8.05	365	16	237.25	180	Colorless	Odorless
57	528087	1462016	HDW10	7.23	755	34	490.75	410	Colorless	Odorless
58	556317	1464712	SHW19	7.41	5040	570	3276	580	Colorless	Odorless
59	557156	1464310	HDW11	7.75	1615	210	1049.75	840	Colorless	Odorless
60	558585	1463302	DW4	7.49	112	40	72.8	470	Colorless	Odorless

Appendix III Chemistry Laboratory Result of Collected Water Samples, cations and anions, Zamra catchment

a) Cations

No	Sample Code	Na^+ (mg/l)	Mg^{2+} (mg/l	Ca^{2+} (mg/l)	K^+ (mg/l)	Fe(mg/l)	Zn(mg/l)	Ag(mg/l)	Cu(mg/l)
1	HDW1	117.880	47.307	68.560	1.631	0.030	0.152	0.036	0.036
2	SHW1	49.104	42.637	101.800	1.853	0.285	0.304	0.025	0.025
3	RV1	31.323	45.454	79.771	0.530	0.079	0.029	0.010	0.010
4	OPW1	44.637	50.118	100.178	1.112	0.111	0.097	0.020	0.020
5	SHW2	51.149	1.457	4.871	0.312	0.042	0.015	0.005	0.005
6	CN1	18.697	19.389	50.653	0.974	0.066	0.026	0.027	0.027
7	SHW3	32.374	18.986	47.839	0.883	0.037	0.064	0.014	0.014
8	DW1	83.157	18.570	1.944	0.254	0.094	0.034	0.026	0.026
9	DM1	23.834	23.490	32.075	2.797	0.293	0.014	0.021	0.021
10	HDW2	11.865	28.2087	34.510	0.388	0.051	0.336	0.008	0.008
11	SHW4	24.978	36.112	51.661	0.732	0.138	0.189	0.120	0.120
12	HDW3	17.703	14.991	47.983	1.032	0.096	0.196	0.027	0.027
13	SHW5	54.446	38.861	101.190	0.946	0.024	0.058	0.008	0.008
14	CN2	42.840	34.355	72.934	1.431	0.101	0.019	0.018	0.018
15	CN3	32.664	27.077	57.552	1.139	0.061	0.028	0.009	0.009
16	CN4	53.825	50.491	106.000	2.404	0.069	0.011	0.021	0.021
17	RV2	53.606	42.643	74.620	1.560	0.023	0.013	0.005	0.005
18	CN5	68.685	44.011	93.407	1.929	0.060	0.051	0.004	0.004
19	SHW6	75.695	21.476	364.046	1.494	0.095	0.330	0.011	0.011
20	SP1	5.678	7.932	61.157	0.193	0.026	0.009	0.002	0.002
21	SP2	67.464	54.754	168.428	2.230	0.022	0.016	0.002	0.002

22	SP4	44.965	47.076	105.902	2.322	0.088	0.014	0.004	0.004
23	SP3	51.960	46.628	124.872	0.491	0.023	0.014	0.004	0.004
24	DW2	35.747	23.639	98.652	1.116	0.022	0.117	0.005	0.005
25	DW3	61.655	29.990	502	4.545	0.319	0.227	0.031	0.031
26	HDW4	28.542	39.550	124.310	0.738	0.023	0.027	0.007	0.007
27	HDW5	47.200	34.998	124.520	1.812	0.212	0.027	0.019	0.019
28	SHW7	31.602	27.356	111.398	1.259	0.076	0.268	0.051	0.051
29	HDW6	86.663	29.990	125.765	2.099	0.072	0.047	0.017	0.017
30	SHW8	17.153	25.363	77.515	0.293	0.053	0.102	0.015	0.015
31	SHW9	42.918	32.718	112.944	0.311	0.022	0.025	0.012	0.012
32	HDW7	39.174	34.794	118.023	1.097	0.022	0.087	0.004	0.004
33	HDW8	25.995	21.552	114.000	0.003	0.025	0.017	0.008	0.008
34	SP5	76.320	32.759	126.784	3.571	0.164	0.161	0.060	0.060
35	OPW2	18.209	13.464	81.607	0.837	0.095	0.009	0.012	0.012
36	SP6	17.811	29.264	114.000	1.839	0.073	0.010	0.025	0.025
37	SP7	68.399	36.949	89.698	0.614	0.024	0.019	0.004	0.004
38	CN6	97.571	62.809	150.008	4.066	0.053	0.021	0.014	0.014
39	SHW10	172.708	19.681	96.164	3.502	0.214	0.112	0.018	0.018
40	SP8	152.933	60.116	484.753	8.708	0.194	0.066	0.013	0.013
41	SHW11	25.141	44.140	83.807	0.747	0.063	0.162	0.019	0.019
42	OPW3	24.620	42.109	77.732	8.144	0.023	0.050	0.016	0.016
43	SHW12	44.306	71.381	102.789	0.548	0.022	0.073	0.010	0.010
44	DM2	21.470	6.966	34.165	1.198	0.211	0.014	0.017	0.017
45	DM3	25.442	8.289	35.179	1.793	0.491	0.014	0.057	0.057
46	SHW13	90.637	51.851	111.000	5.108	0.021	0.008	0.003	0.003
47	SP9	12.031	13.531	52.018	1.010	0.040	0.013	0.004	0.004
48	SHW14	111.740	82.488	132.258	15.084	0.023	0.048	0.007	0.007
49	SHW15	175.918	129.650	162.721	12.452	0.021	0.086	0.004	0.004
50	RV3	85.179	70.438	140.131	2.712	0.024	0.036	0.003	0.003
51	SHW16	30.945	45.664	132.357	3.774	0.020	0.032	0.003	0.003
52	SHW17	33.235	38.997	124.851	12.175	0.021	0.016	0.003	0.003
53	HDW9	10.453	5.627	26.288	1.995	0.273	0.079	0.011	0.011
54	SHW18	18.605	66.811	210.471	5.097	0.021	0.016	0.003	0.003
55	CD1	26.102	64.604	344.913	2.910	0.025	0.012	0.002	0.002
56	DM4	11.917	12.943	68.253	1.880	0.075	0.014	0.002	0.002
57	HDW10	20.887	30.549	145.478	1.103	0.022	0.009	0.004	0.004
58	SHW19	806.782	148.629	343.438	9.199	0.021	0.409	0.005	0.005
59	HDW11	153.495	72.666	145.819	4.353	0.022	0.125	0.004	0.004
60	DW4	64.366	58.589	124.520	2.511	0.020	0.054	0.003	0.003

b) Anions

No	Sample Code	HCO_3^-(mg/l)	CO_3^{2-}(mg/l)	SO_4^{2-}(mg/l)	NO_3^-(mg/l)	NH_3(mg/l)
1	HDW1	793	0	10	0.01	0.09
2	SHW1	671	0	20	0.07	0.08
3	RV1	610	0	14	0.11	0.08
4	OPW1	488	0	69	0.23	0.07
5	SHW2	42.70	47.998	20	0.05	0.08
6	CN1	152.5	30	9	0.43	0.02
7	SHW3	335.5	0	47	0.5	0.12
8	DW1	0	149.998	9	0.31	0.17
9	DM1	30.5	60	31	0.02	0.15
10	HDW2	366	0	19	0.34	0.16
11	SHW4	439.2	0	110	0.03	0.08
12	HDW3	213.5	0	25	0.04	0.09
13	SHW5	427	0	15	0.14	0.13
14	CN2	158.6	72	39	0.46	0.08
15	CN3	195.2	60	24	0.05	0.08
16	CN4	189.1	48	160	0.34	0.07
17	RV2	335.5	30	41	0.5	0.15
18	CN5	445.3	0	64	0	0.11
19	SHW6	274.5	0	730	0.13	0.13
20	SP1	335.5	0	170	0.33	0.1
21	SP2	463.6	0	160	0.29	0.14
22	SP4	390.4	0	110	0.08	0.11
23	SP3	579.5	0	64	0.25	0.09
24	DW2	445.3	0	100	0.06	0.17
25	DW3	292.8	0	800	0.24	0.08
26	HDW4	439.2	0	90	1.12	0
27	HDW5	469.7	0	160	0.01	0.1
28	SHW7	390.4	0	15	0	0.15
29	HDW6	317.2	0	110	0.43	0.34
30	SHW8	427	0	43	1.06	0.03
31	SHW9	463.6	0	110	0.03	0.08
32	HDW7	451.4	0	150	0	0.15
33	HDW8	445.3	0	27	0.08	0.09
34	SP5	366	0	54	0.9	0.16
35	OPW2	311.1	0	57	0.62	0.066
36	SP6	305	0	26	0.95	0.07
37	SP7	488	0	90	0.11	0.16
38	CN6	30.5	42	520	0.01	0.21
39	SHW10	195.2	0	400	0.01	0.36
40	SP8	122	0	1360	0.02	0.18
41	SHW11	457.5	0	4	0.04	0.15
42	OPW3	610	30	57	0.05	0.03
43	SHW12	579.5	0	73	0.34	0.31

44	DM2	0	53.99	68	0.02	0.07
45	DM3	0	59.98	52	0	0.15
46	SHW13	518.5	0	50	1.11	0
47	SP9	195.2	0	13	1.3	0.07
48	SHW14	542.9	0	80	0.16	0.19
49	SHW15	701.5	0	530	0.48	0.1
50	RV3	274.5	0	410	0.02	0.08
51	SHW16	408.7	0	64	0.01	0.01
52	SHW17	396.5	0	60	1.03	0.09
53	HDW9	67.1	0	2	0.01	0.14
54	SHW18	427	0	140	0.16	0.08
55	CD1	347.7	0	680	0.09	0.08
56	DM4	152.5	0	56	1.12	0.1
57	HDW10	396.5	0	63	1.12	0
58	SHW19	274.5	0	130	0.65	0.22
59	HDW11	439.2	0	26	0.61	0.07
60	DW4	366	0	290	0	0.1

Appendix IV: Water-types and Charge Error Balance, Zamra catchment

No	Sample Code	Water Type	CEB (%)
1	HDW1	Na-Mg-Ca-HCO3	-8.015097
2	SHW1	Ca-Mg-HCO3	-6.536586
3	RV1	Ca-Mg-HCO3	-11.15219
4	OPW1	Ca-Mg-HCO3	1.671471
5	SHW2	Na-CO3-HCO3	-8.770905
6	CN1	Ca-Mg-HCO3-CO3	6.838473
7	SHW3	Ca-Mg-Na-HCO3	-13.105
8	DW1	Na-Mg-CO3	-4.746723
9	DM1	Mg-Ca-Na-CO3	12.87922
10	HDW2	Mg-Ca-HCO3	-19.84087
11	SHW4	Mg-Ca-HCO3-SO4	-19.02081
12	HDW3	Ca-Mg-HCO3	-0.6085694
13	SHW5	Ca-Mg-Na-HCO3	13.94979
14	CN2	Ca-Mg-Na-HCO3-CO3	11.19536
15	CN3	Ca-Mg-Na-HCO3-CO3	-0.4553396
16	CN4	Ca-Mg-Na-SO4-HCO3	11.16336
17	RV2	Ca-Mg-Na-HCO3	7.779224
18	CN5	Ca-Mg-Na-HCO3	7.33479
19	SHW6	Ca-SO4-HCO3	3.964529
20	SP1	Ca-HCO3-SO4	-42.15872
21	SP2	Ca-Mg-Na-HCO3-SO4	12.52527
22	SP4	Ca-Mg-HCO3-SO4	6.966428
23	SP3	Ca-Mg-HCO3	1.494173
24	DW2	Ca-Mg-HCO3-SO4	-9.843517
25	DW3	Ca-SO4	15.15982

26	HDW4	Ca-Mg-HCO3	-1.132449
27	HDW5	Ca-Mg-HCO3-SO4	-1.835813
28	SHW7	Ca-Mg-HCO3	8.000423
29	HDW6	Ca-Na-Mg-HCO3-SO4	15.13169
30	SHW8	Ca-Mg-HCO3	-11.66143
31	SHW9	Ca-Mg-HCO3-SO4	0.0648276
32	HDW7	Ca-Mg-HCO3-SO4	5.340328
33	HDW8	Ca-Mg-HCO3	0.5645615
34	SP5	Ca-Na-Mg-HCO3	22.92917
35	OPW2	Ca-HCO3	-6.387073
36	SP6	Ca-Mg-HCO3	15.09897
37	SP7	Ca-Mg-Na-HCO3	-5.119501
38	CN6	Ca-Mg-Na-SO4-Cl	2.571484
39	SHW10	Na-Ca-SO4-HCO3	-1.446063
40	SP8	Ca-SO4	6.138987
41	SHW11	Ca-Mg-HCO3	3.814586
42	OPW3	Ca-Mg-HCO3	-21.62096
43	SHW12	Mg-Ca-HCO3	1.74579
44	DM2	Ca-Na-CO3-SO4	-3.874116
45	DM3	Ca-Na-CO3-SO4-Cl	5.245356
46	SHW13	Ca-Mg-Na-HCO3	9.849202
47	SP9	Ca-Mg-HCO3	-0.2802899
48	SHW14	Mg-Ca-Na-HCO3-Cl	14.31871
49	SHW15	Mg-Ca-Na-HCO3-SO4	2.979072
50	RV3	Ca-Mg-Na-SO4-HCO3	5.775631
51	SHW16	Ca-Mg-HCO3	12.56468
52	SHW17	Ca-Mg-HCO3	12.69531
53	HDW9	Ca-Mg-Na-HCO3	22.89985
54	SHW18	Ca-Mg-HCO3-SO4	21.71853
55	CD1	Ca-Mg-SO4-HCO3	7.172941
56	DM4	Ca-Mg-HCO3-SO4	9.772171
57	HDW10	Ca-Mg-HCO3	9.815823
58	SHW19	Na-Ca-Mg-Cl	46.90301
59	HDW11	Ca-Na-Mg-HCO3-Cl	18.74212
60	DW4	Ca-Mg-Na-SO4-HCO3	2.617343

Appendix V: Ionic Ratio used in source rock deduction

No	Sample Code	Ca^{2+}/Mg^{2+} (Meq/l)	Na^{+}/Cl^{-} (meq/l)	(Ca +Mg) (meq/l)	(SO4 + HCO3) (meq/l)	(Na -Cl) (meq/l)
1	HDW1	0.88	0.88	7.31	13.21	3.717009
1	HDW1	0.88	0.88	8.59	11.21	1.289631
2	SHW1	1.45	1.45	7.72	10.42	0.290515
3	RV1	1.06	1.06	9.12	8.29	0.672184
4	OPW1	1.21	1.21	0.36	2.14	1.858115
5	SHW2	2.03	2.03	4.12	2.92	0.192662
6	CN1	1.58	1.58	3.95	5.69	0.900441
7	SHW3	1.53	1.53	1.63	0.98	3.052937
8	DW1	0.06	0.06	3.53	0.69	0.61356
9	DM1	0.83	0.83	4.04	6.65	0.092947
10	HDW2	0.74	0.74	5.55	7.60	0.804372
11	SHW4	0.87	0.87	3.63	5.79	0.318683
12	HDW3	1.94	1.94	8.25	7.52	1.663011
13	SHW5	1.58	1.58	6.47	2.91	1.017145
14	CN2	1.29	1.29	5.10	4.01	0.518118
15	CN3	1.29	1.29	9.44	3.60	0.930813
16	CN4	1.27	1.27	7.23	8.83	1.485462
17	RV2	1.06	1.06	8.28	8.15	1.859254
18	CN5	1.29	1.29	19.93	5.83	1.543577
19	SHW6	10.28	10.28	3.70	20.70	-0.43005
20	SP1	4.68	4.68	12.91	11.14	1.524078
21	SP2	1.87	1.87	9.16	9.73	0.940319
22	SP4	1.36	1.36	10.07	11.79	1.131775
23	SP3	1.62	1.62	6.87	8.63	0.652195
24	DW2	2.53	2.53	27.52	6.88	1.83554
25	DW3	10.15	10.15	9.46	23.86	-0.62026
26	HDW4	1.91	1.91	9.09	9.57	1.488877
27	HDW5	2.16	2.16	7.81	9.73	0.246256
28	SHW7	2.47	2.47	8.74	5.51	2.020637
29	HDW6	2.54	2.54	5.96	9.29	0.181919
30	SHW8	1.85	1.85	7.31	13.21	3.717009
31	SHW9	2.09	2.09	8.33	8.50	1.584719
32	HDW7	2.06	2.06	8.75	9.69	0.575607
33	HDW8	3.21	3.21	7.46	10.42	0.510137
34	SP5	2.35	2.35	9.02	6.56	2.699112
35	OPW2	3.68	3.68	5.18	6.22	0.28428
36	SP6	2.36	2.36	8.10	6.19	-0.24078
37	SP7	1.47	1.47	7.52	8.54	1.226224
38	CN6	1.45	1.45	12.65	2.37	0.859015
39	SHW10	2.96	2.96	6.42	14.03	4.691419
40	SP8	4.89	4.89	29.14	10.33	5.241697
41	SHW11	1.15	1.15	7.81	35.82	0.416571
42	OPW3	1.12	1.12	7.34	10.08	-0.11386

43	SHW12	0.87	0.87	11.00	10.69	0.460318
44	DM2	2.97	2.97	2.28	1.52	0.651812
45	DM3	2.57	2.57	2.44	1.42	0.203973
46	SHW13	1.30	1.30	9.81	9.58	2.137102
47	SP9	2.33	2.33	3.71	4.24	-0.26654
48	SHW14	0.97	0.97	13.39	9.17	1.47533
49	SHW15	0.76	0.76	18.79	13.17	5.000305
50	RV3	1.21	1.21	12.79	15.53	2.012505
51	SHW16	1.76	1.76	10.36	15.24	0.217674
52	SHW17	1.94	1.94	9.44	7.83	0.542968
53	HDW9	2.83	2.83	1.77	2.35	0.172595
54	SHW18	1.91	1.91	16.00	7.04	-0.14982
55	CD1	3.24	3.24	22.53	8.61	0.458375
56	DM4	3.20	3.20	4.47	16.66	0.066994
57	HDW10	2.89	2.89	9.77	7.67	-0.05056
58	SHW19	1.40	1.40	29.37	5.81	19.01375
59	HDW11	1.22	1.22	13.26	9.91	0.752743
60	DW4	1.29	1.29	11.04	6.54	1.671394

Appendix VI: Saturation index of water samples (-ve indicates dissolution and +ve indicates precipitation)

No.	Sample code	Calcite	Aragonite	Dolomite	Siderite	Rhodochrosite	Witherite	Gypsum	Anhydrite
1	HDW1	3.316	3.168	6.611	1.507	1.233	-0.243	-0.728	-0.943
2	SHW1	2.798	2.648	5.281	1.842	2.018	0.575	-0.144	-0.368
3	RV1	3.59	3.441	7.052	2.08	1.106	1.098	-0.42	-0.644
4	OPW1	3.027	2.883	5.945	1.756	0.92	0.097	0.384	0.18
5	SHW2	2.883	2.735	5.46	1.244	0.535	1.813	-1.395	-1.634
6	CN1	3.584	3.435	6.868	2.148	1.059	1.091	-0.463	-0.7
7	SHW3	2.873	2.728	5.498	1.432	0.425	0.568	0.097	-0.119
8	DW1	2.465	2.321	6.234	0.957	1	1.449	-2.095	-2.31
9	DM1	3.602	3.459	7.347	2.531	1.958	1.311	-0.292	-0.508
10	HDW2	2.791	2.645	5.621	1.578	0.483	-0.256	-0.402	-0.625
11	SHW4	2.981	2.834	5.943	2.079	0.437	-0.634	0.341	0.123
12	HDW3	2.081	1.935	3.772	1.133	0.465	-0.372	0.02	-0.204
13	SHW5	2.929	2.782	5.563	0.945	0.285	-0.6	-0.153	-0.375
14	CN2	3.882	3.736	7.66	2.437	1.024	0.826	0.042	-0.178
15	CN3	3.792	3.649	7.532	2.234	1.05	1.081	-0.281	-0.49
16	CN4	3.851	3.709	7.614	2.264	1.343	0.43	0.727	0.529
17	RV2	3.686	3.541	7.332	1.69	0.988	0.267	0.065	-0.149
18	CN5	3.625	3.481	7.125	2.019	1.332	0.704	0.313	0.104
19	SHW6	3.081	2.936	5.072	1.532	0.986	-1.183	1.765	1.562
20	SP1	2.643	2.496	4.496	1.059	0.025	-0.261	0.649	0.425
21	SP2	2.901	2.757	5.484	0.77	0.714	-0.491	0.907	0.7
22	SP4	2.975	2.83	5.739	1.621	0.583	-0.448	0.653	0.437
23	SP3	3.03	2.88	5.82	0.98	0.79	-0.46	0.4	0.19
24	DW2	2.97	2.83	5.49	1.03	0.15	-0.5	0.57	0.36
25	DW3	3.45	3.31	5.83	2.28	2.15	-1.05	1.91	1.71
26	HDW4	2.93	2.78	5.52	0.91	0.32	-0.84	0.62	0.41
27	HDW5	3.04	2.89	5.68	2	0.4	-0.43	0.8	0.59
28	SHW7	3.04	2.89	5.63	1.53	0.4	-0.3	-0.1	-0.31
29	HDW6	2.97	2.82	5.45	1.49	0.38	-0.3	0.77	0.55
30	SHW8	3.13	2.98	6.02	1.62	0.85	0.1	0.16	-0.06
31	SHW9	3.04	2.89	5.67	1.02	0.25	-0.75	0.65	0.43
32	HDW7	3	2.85	5.6	1.01	0.36	-0.02	0.78	0.56
33	HDW8	3	2.85	5.43	1	0.6	-0.64	0.13	-0.08
34	SP5	3.07	2.92	5.67	1.87	1.12	-0.62	0.48	0.26
35	OPW2	2.98	2.83	5.28	1.74	0.73	-1.03	0.43	0.2
36	SP6	3.11	2.97	5.95	1.58	0.81	0	0.21	-0.01
37	SP7	3.3	3.15	6.37	1.37	0.68	-0.38	0.44	0.23
38	CN6	3.84	3.7	7.44	2.03	0.99	0.44	1.32	1.11
39	SHW10	3.17	3.02	5.77	2.43	1.39	-1.03	1.07	0.86
40	SP8	3.28	3.13	5.76	2.09	1.97	-1.62	2.14	1.94
41	SHW11	3.16	3.01	6.14	1.62	0.66	-0.09	-0.8	-1.03

42	OPW3	3.77	3.62	7.43	1.7	1.85	0.83	0.05	-0.17
43	SHW12	3.1	2.95	6.17	1.08	0.53	-0.19	0.38	0.16
44	DM2	3.58	3.43	6.66	0.84	1.57	0.68	0.17	-0.07
45	DM3	3.7	3.56	7.02	-1.17	2.09	0.84	-0.07	-0.3
46	SHW13	3.44	3.3	6.8	1.37	1.14	0.82	0.23	0.04
47	SP9	2.2	2.06	3.98	0.85	0.46	-0.08	-0.21	-0.42
48	SHW14	2.96	2.82	5.96	0.91	0.7	0.06	0.46	0.27
49	SHW15	2.93	2.79	6.03	0.92	1.9	-0.49	1.13	0.96
50	RV3	3.46	3.31	6.76	1.54	0.59	0.13	1.19	0.98
51	SHW16	3.1	2.95	5.94	1	0.54	0.32	0.5	0.3
52	SHW17	2.94	2.8	5.58	0.9	1.35	-0.1	0.47	0.27
53	HDW9	1.65	1.5	2.74	1.55	0.66	-0.43	-0.94	-1.17
54	SHW18	2.97	2.83	5.61	0.73	0.32	-0.67	0.96	0.75
55	CD1	3.67	3.53	6.77	1.47	0.59	-0.23	1.68	1.48
56	DM4	3.24	3.1	5.9	2.01	0.81	0.73	0.47	0.25
57	HDW10	3.01	2.87	5.49	0.9	0.18	0.03	0.58	0.37
58	SHW19	3.403	3.259	6.674	1.079	1.118	-0.676	1.042	0.852
59	HDW11	3.55	3.4	6.99	1.37	0.83	0.57	0.1	-0.11
60	DW4	3.06	2.91	5.93	1.09	0.57	-0.16	1.02	0.81

No.	Sample code	Barite	Hematite	Goethite	Fe (OH)3	Pyrolusite	Manganite	Pyrochrosite	K-Jarosite
1	HDW1	1.093	10.558	4.696	-1.414	-18.411	-9.22	-6.86	-12.736
2	SHW1	3.032	3.772	1.005	8.374	3.797	-20.007	-23.287	-14.18
3	RV1	2.47	2.619	-0.134	13.082	6.037	-17.653	-20.556	-16.16
4	OPW1	2.779	2.946	0.255	10.333	4.166	-18.939	-23.066	-14.7
5	SHW2	2.904	0.068	-2.686	19.255	9.142	-12.79	-12.051	-19.22
6	CN1	2.418	1.563	-1.194	16.065	7.569	-15.857	-16.936	-17.1
7	SHW3	3.125	10.763	4.508	-1.453	-18.825	-10.086	-7.536	-10.751
8	DW1	2.195	19.55	8.726	2.855	-11.155	-4.211	-2.975	-5.226
9	DM1	2.727	20.755	9.365	3.475	-11.591	-4.767	-3.827	-0.273
10	HDW2	1.902	10.886	4.727	-1.31	-19.037	-9.985	-7.465	-11.663
11	SHW4	2.077	12.077	5.284	-0.737	-18.868	-9.967	-7.517	-8.478
12	HDW3	2.91	7.374	2.919	-3.091	-21.084	-11.356	-8.046	-13.922
13	SHW5	1.677	8.068	3.355	-2.702	-20.424	-10.929	-8.049	-14.856
14	CN2	2.322	17.832	8.08	2.102	-14.567	-6.926	-5.556	-3.615
15	CN3	2.317	17.458	7.664	1.798	-14.251	-7.068	-5.658	-4.625
16	CN4	2.602	17.041	7.324	1.519	-14.217	-7.119	-5.509	-3.064
17	RV2	1.979	14.213	6.218	0.264	-16.044	-8.067	-6.247	-7.743
18	CN5	2.72	13.897	6	0.073	-16.337	-8.258	-6.208	-7.167
19	SHW6	2.849	9.812	4.037	-1.934	-19.223	-10.097	-7.177	-9.112
20	SP1	3.108	8.867	3.795	-2.281	-20.334	-10.871	-8.111	-12.498
21	SP2	2.851	7.181	2.671	-3.273	-20.136	-10.963	-7.883	-13.478
22	SP4	2.575	10.104	4.245	-1.75	-19.498	-10.392	-7.622	-10.139

23	SP3	2.24	8.06	3.06	-2.86	-19.6	-10.7	-7.78	-13.99
24	DW2	2.43	8.83	3.5	-2.45	-19.84	-10.96	-8.17	-12.38
25	DW3	2.75	12.33	5.21	-0.72	-17.22	-8.49	-5.79	-5.56
26	HDW4	2.19	7.97	3.11	-2.85	-20.19	-11.06	-8.12	-13.54
27	HDW5	2.68	10.64	4.46	-1.51	-19.75	-10.73	-7.93	-9.08
28	SHW7	1.9	9.83	4.03	-1.93	-19.67	-10.69	-7.87	-12.36
29	HDW6	2.84	9.9	4.17	-1.84	-19.74	-10.55	-7.75	-10.43
30	SHW8	2.47	10.17	4.08	1.55	-13.77	-10.65	-9.02	-10.62
31	SHW9	2.22	8.68	3.57	-2.44	-19.99	-10.8	-8.03	-13.1
32	HDW7	3.12	8.54	3.52	-2.51	-19.99	-10.74	-7.94	-12.43
33	HDW8	1.84	8.33	3.32	-2.66	-19.81	-10.67	-7.79	-16.53
34	SP5	2.15	10.57	4.54	-1.48	-19.07	-9.82	-7.04	-9.82
35	OPW2	1.78	10.86	4.81	-1.27	-19.2	-9.83	-7.21	-10.18
36	SP6	2.44	10.06	4.06	1.04	-14.6	-10.61	-8.82	-10.88
37	SP7	2.11	10.85	4.6	-1.39	-18.4	-9.69	-7.28	-10.81
38	CN6	3.25	19.3	8.76	2.81	-13.14	-5.85	-4.72	0.03
39	SHW10	2.22	14.85	6.6	0.61	-16.49	-8.04	-5.88	-3.72
40	SP8	2.59	13.41	5.81	-0.16	-16.56	-7.89	-5.38	-3.83
41	SHW11	1.31	10.51	4.64	-1.45	-19.29	-9.95	-7.38	-13.28
42	OPW3	2.49	13.43	6.11	0.01	-15.96	-7.38	-5.58	-7.86
43	SHW12	2.46	8.72	3.66	-2.39	-19.81	-10.51	-7.79	-13.31
44	DM2	2.61	20.33	9.46	3.42	-10.38	-3.43	-3.03	-2.03
45	DM3	2.41	19.82	9.17	3.15	-7.41	-1.18	-1.44	-4.82
46	SHW13	2.91	11.24	4.39	-1.4	-17.2	-9.35	-6.91	-10.01
47	SP9	2.83	7.37	2.69	-3.21	-20.45	-11.25	-7.99	-14.78
48	SHW14	2.87	7.94	2.73	-3.06	-19.44	-11	-7.97	-12.46
49	SHW15	3.03	7.37	2.43	-3.36	-18.58	-10.11	-7	-11.7
50	RV3	3.2	13	5.59	-0.36	-17.19	-8.94	-6.8	-6.74
51	SHW16	3.03	9.03	3.37	-2.46	-19.06	-10.62	-7.79	-12.04
52	SHW17	2.73	8.3	3	-2.83	-18.64	-10.08	-7.11	-12.25
53	HDW9	2.32	9.19	3.83	-2.18	-20.4	-10.68	-7.37	-12.9
54	SHW18	2.65	7.15	2.68	-3.28	-20.54	-11.31	-8.22	-13.3
55	CD1	3.13	11.79	4.96	-0.98	-17.92	-9.49	-7.12	-7.58
56	DM4	3.29	14.53	6.41	0.44	-16.7	-8.39	-6.3	-5.99
57	HDW10	2.95	8.08	3.26	-2.75	-20.37	-11.07	-8.16	-13.56
58	SHW19	2.317	10.127	4.146	-1.809	-18.232	-9.393	-6.663	-10.452
59	HDW11	2.46	11.3	4.72	-1.22	-17.86	-9.39	-7	-10.72
60	DW4	3.15	9.63	3.98	-2	-19.06	-10.14	-7.49	-10.48