**ORIGINAL ARTICLE**

# Hydrogeochemical studies of groundwater in semi-arid areas of northern Ethiopia using geospatial methods and multivariate statistical analysis techniques

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## Abstract

The present study focused on evaluating the groundwater hydrogeochemical of shallow aquifers in the semi-arid areas of northern Ethiopia, using geospatial modelling and multivariate statistical techniques. Physico-chemical parameters, including pH, major ions, electrical conductivity (EC), total dissolved solids (TDS), total hardness (TH), pollution index (PI) and other parameters, from 22 samples have been used to assess water quality, sources of various ions, water types and factors controlling groundwater chemistry. Results showed that the spatial distribution of major ions, EC, TDS, TH and PI values in these samples significantly differ from one location to another due to geological variations and anthropogenic activities of the area. The quality of most groundwater is generally unfit for drinking due to their PI, EC, TH, calcium, potassium, total iron and bicarbonate ($HCO_3^-$) values that found to be above the permissible limits of WHO and Ethiopian standards. The parameters like sodium percentage, sodium adsorption ratio (SAR), residual sodium bicarbonate, permeability index, magnesium hazard and Kelly's ratio revealed good quality of groundwater for irrigation utilization, whereas EC of irrigation water (ECiw), combined effects of ECiw − SAR and bicarbonate hazard values indicated that majority of groundwater are not suitable for irrigation use. Piper trilinear diagram classified majority of samples under temporary hardness with Ca–Mg–$HCO_3$ type. Further, Gibbs diagram reveals that water–rock interaction is the major hydrogeochemical processes governing the water chemistry of the study area. Therefore, it is recommended to perform a constant water quality checking program and improvement of tangible management practices for sustainable utilization of groundwater resou*rces.*

**Keywords** Hydrochemistry · Spatial distribution · Multivariate statistical analysis · Water quality · Gergera

## Introduction

Over 70% of the planet's total freshwater is positioned in the sub-surface; however unregulated and unrestrained withdrawal of this groundwater resource can lead changes in aquifer system (Kallioras et al. 2013). As is the case all over Tigray, satisfying the demands of agriculture, industry and a growing population has exerted pressure upon groundwater resource in Ethiopia (Kawo and Karuppannan 2018). Considering the

societal and ecological importance and usage of groundwater resource has a lot to do with its quality and chemistry (Idowu et al. 2017). In addition to the anthropogenic effects, groundwater stored in aquifer is also affected by geological structure, geochemical processes such as rock-water interaction within the aquifer system and constituents of precipitation which percolates into the aquifer (Salifu et al. 2017; Dişli 2018). Groundwater quality affects supply of drinkable fresh water which is directly linked with human health. Agriculture is vital to Ethiopia's prosperity because about 85% of the greater than 100 million populations with a growth rate of 2.6% are engaged in it. Although agricultural production in Ethiopia has significantly increased food security, it has also damaged water resources. Hence, to manage and sustain water resources efficiently and forecast the change in groundwater chemistry, it is necessary to understand the hydrogeochemical characteristics of the groundwater and its development under natural water flow procedures. The groundwater chemistry depends on a

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number of factors such as variations in nature of geochemical reactions, inputs from sources other than water–rock interaction, general geology, rate and amount of groundwater flow and solubility of salts (Amiri et al. 2015; Gan et al. 2018). Evaluating groundwater characteristics using hydrogeochemical methods were reported in different parts of the world, for instance, by Li et al. (2014) in northwest China, Tesoriero et al. (2004) in the south eastern United States, Möller et al. (2007) in the lower Jordan valley and in the Dead Sea area and Wen et al. (2008) in north-western China are some of the groundwater studies reported by applying hydrogeochemical methods. The increasing exploitation and unsustainable intensification of production to support population growth by using mixed agriculture frequently can accelerate deterioration in groundwater quality in the northern parts of Ethiopia, particularly in Tigray. To minimize future food insecurity in the country, sustainable quantity and quality of groundwater become a vital to attain the radical increase in agricultural growth and to avoid the expected deterioration of groundwater quality due to extensive abstraction for various uses.

Gergera watershed, parts of Tigray region in eastern zone, is intensively inhabited and overgrazed, leading to increase agricultural area. The semi-aridity and agricultural economic dependency are the main cause for the high demand for water which is gradually achieved by groundwater over-abstraction. For this continual decline of groundwater reservoir as well as deterioration of water quality of the watershed, it is necessary to monitor the groundwater chemistry in order to maintain the groundwater resources and agricultural development in this watershed. So far, the hydrochemistry, geochemical interactions and the suitability of the groundwater for drinking and agricultural purposes have not been studied in great detail in the watershed. Hence, the purposes of the present study are: (1) to determine the physico-chemical and geospatial distributions of groundwater parameters, (2) to evaluate the groundwater suitability for drinking and agricultural uses by applying various indices and (3) to evaluate hydrogeochemistry and geochemical interaction processes controlling groundwater hydrochemistry. The results of the study will be useful for sustainable management of groundwater resources according to the water chemistry and enable planners and policy makers to develop a strategy to solve problems in the region as well as similar problems in elsewhere.

## Materials and methods

### Study area description

The study was held at Gergera watershed (900 ha), located in the Eastern Zone of Tigray Regional State, in Atsbi Wenberta, Northern part of Ethiopia, at about 65 km northeast of Mekelle. Geographically, the study area is situated between 39°30' and 39°45'E and 13°30'–13°45'N. The area is located within the Tigray plateau of the northern highlands and lowlands physiographic unit of the country (Fig. 1).

The Tigray highlands lying in the northern part of the country are generally known for their rugged topography, mountainous landscapes which govern the variations in regional geomorphology, water quality, ecological zoning system soil classifications, extent and quality of plant and as well as animal life. The district of the study area lies within the sub-tropical agro-climatic zone and its altitude ranges from 1500 to 2800 m (m) above sea level. The mean annual rainfall of the study area is 574.141 mm. Rainfall is a major factor controlling the surface and subsurface hydrology of the area. The amount of annual rainfall affects the type of vegetation cover and stream and spring discharge and volume of the groundwater. The highest value of the mean annual minimum temperature is 8.5 °C and the lowest value of the mean annual minimum temperature is 6.3 °C, whereas the highest and lowest values of mean annual maximum temperatures are 31.45 and 30.15 °C, respectively. The mean annual air temperature of the watershed is 19.7 °C, and the yearly average maximum and minimum temperature is 22.0 °C (in June) and 17.0 °C (in December), respectively. The annual variation of temperature is thus 5 °C.

Agriculture is principal occupation of the people and is backbone of Ethiopia's economy. Rain-fed farmlands, irrigated farmlands, grasslands, bare lands with scattered trees and bushes, and built-up areas were identified as major land use types in the study area (Hailu and Teka 2020). During rainy season, crops such as wheat (*Triticum aestivum*), barley (*Hordeum vulgare*), maize (*Zea mays*), beans (*Phaseolus vulgaris*) and peas (*Pisum sativum*) are mainly cultivated in both rain-fed and irrigated farm lands. However, the major crops grown during the irrigation season are vegetables such as potatoes (*Solanum tuberosum*), tomato (*Solanum lycopersicum*), onion (*Allium cepa*), lettuce (*Lactuca sativa*), hot pepper (*Capsicum frutescens*) and cabbage (*Brassica oleracea*). The lower catchment is the only area where cultivation in the dry season is possible twice a year using irrigation (water from hand-dug wells) but with low yield gain. To maximize agricultural yield, local farmers use fertilizers such as urea and di-ammonium phosphates. These can contribute towards the raise of saline content via salinization processes directly or indirectly. Traditional flooding irrigation is a main irrigation type in the study area, causing in the loss of nutrients in soils and high nutrients in drainage groundwater. Farmland drainage with high nutrients may percolate into shallow aquifer, affecting the hydrogeochemistry of groundwater (Li et al. 2016). In the district (Atsbi Wenberta) there are about 136,139 populations of these 122,769 (90.18%) are rural population and 13,370 (9.81) that of urban populations (Census 2017). Livestock rearing
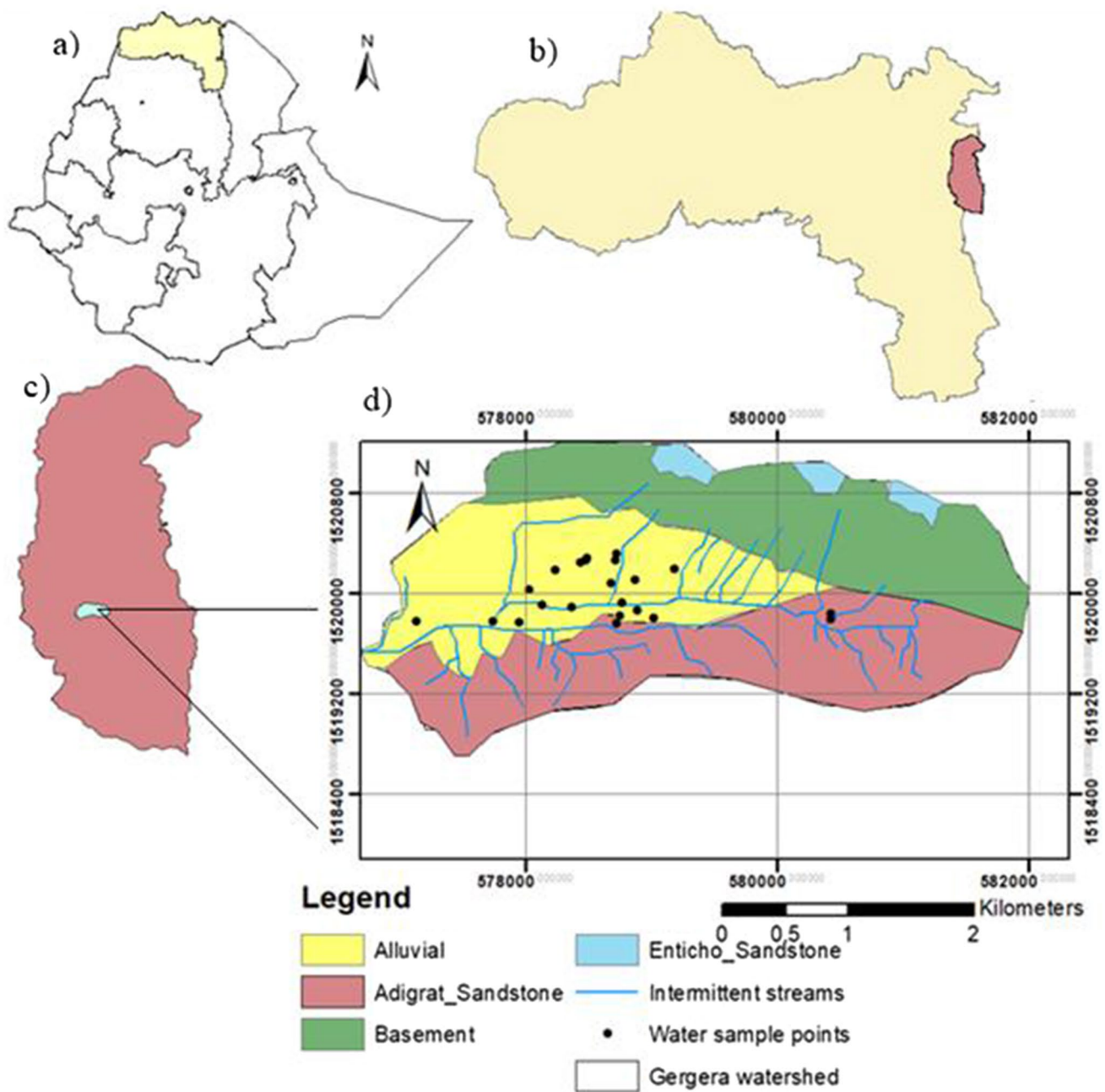
**Fig. 1** Location of the study area: **a** Ethiopia, **b** Tigray indicating Atsbi Wemberta district, **c** Atsbi Wemberta indicating Gergera watershed in sub-district, and **d** Gergera watershed indicating geological classification, as well as intermittent streams and water sampling points

is another important activity in the catchment and includes cattle, goat, sheep, donkey and bees. Bees and sheep are the main animal husbandry to support the crop production.

Geologically the area is characterized by Adigrat Sandstone, metavolcanics, Enticho Sandstone and alluvial sediments. It has small depressed area that extends from South East to North-West bordered by two adjacent highlands (Fig. 1). The maximum peak is found in the southern part of the study area outcropped with the Adigrat Sandstone

and the lowest part is found at the central part of the main drainage line at which the fine grained soil was deposited. The wells are located on the unconsolidated alluvial sediments of the area. The unconsolidated alluvial sediments are highly productive aquifers of the study area while the consolidated rocks are none productive aquifers. That is why most groundwater samples are situated in the plain alluvial deposits of the watershed (Fig. 1).

## Groundwater sampling and physico-chemical analysis

To investigate the water chemistry, twenty-two groundwater samples were collected from boreholes (with $30-54$ m water level depth), open hand-dug (with $5-10$ m water level depth) wells and contact springs during December 2017. After $10-20$ min of pumping, water samples were collected in small cleaned polyethylene bottles and the parameters like EC, $O_2$, pH and temperature were measured in situ at the time of sample collection. After collecting the groundwater samples, the polyethylene bottles were labeled correctly for identification and packed in chiller box and transported to the laboratory for analysis. The location, coordinates and elevation of the sampling position of the groundwater samples of each site were collected using Garmin handheld GPS receiver ($\pm 5$ m or better accuracy). The groundwater samples were stored at 4 °C refrigerator chiller until their laboratory analysis. Water samples were analyzed in the Geochemistry Analytical Laboratory of Earth Sciences department at Mekelle University. Filtered and acidified water samples ($< 0.45$ μm) were analyzed for cations using ICP-90 system. Anions were analyzed from unfiltered water samples using an ion chromatography method. Before cations and anions analyses, the samples were again pre-checked and tested for EC, pH, and temperature in the laboratory to cross check the data. Iron and manganese were analyzed with an atomic absorption spectrophotometer separately. The $HCO_3^-$ of the groundwater was calculated as sum of conservative cations minus sum of conservative anions in the analyzed sample parameters considering the pH ranges (6.8 to 8.2) in the study area and the carbonic acid dissociation stage in the bicarbonate stage as explained by Walton WC (1970). The important anion is $HCO_3^-$ rather than the $CO_3^{2-}$ in all groundwater samples, bcause all $CO_3^{2-}$ are gone at pH less than or equal to 8.3. All the pH values are also greater than 3.82. Therefore, consideration for the concentration of $H^+$ is not important in the ions balance calculation as it is very low. The concentration of $OH^-$ ions in solution is about 7 in the orders of magnitude lower compared to the $H^+$ ions. This is also insignificant to consider in the ionic balance. After physiochemical analysis, the accuracy of the analysis results was checked through charge balance using Eq. (1) as Gidey (2018) reported. And the analysis results were accurate and can be used for the study as the maximum relative error of the results is within the acceptable error limit ($\pm 5\%$). The total permanent hardness of groundwater, which is basically the concentration of calcium and magnesium ions expressed as equivalent of calcium carbonate (Kaur et al. 2017) was also calculated as the molar mass of $CaCO_3$, $Ca^{2+}$ and $Mg^{2+}$ are 100.1, 40.1 and 24.3 g mol$^{-1}$ respectively. The ratios of molar masses of ($CaCO_3 /Ca^{2+}$) is 2.5 and ($CaCO_3 /Mg^{2+}$) is 4.1. Therefore, the total permanent water hardness expressed as equivalent of $CaCO_3$ was calculated using Eq. (2). In addition to the total hardness, the total dissolved solids (TDS) are also the main parameters which are used to assess the water quality for drinking purposes (Davis and Dewiest 1967).

The overall quality of water can be described using Pollution Index (*PI*). PI is a method of rating that tells us the combined influence of each parameter. PI has value starting from 0 to 5 or above, reflecting the relative importance of individual quality parameter and divided by the recommended standard (*Si*) for the maximum plus the minimum values and the summation divided by two as shown by Eq. (3) (Amiri et al. 2015).

Where $C_i$ represents values of the water quality parameter obtained from the laboratory analysis and $S_i$ represents values of the water quality parameter obtained from recommended standards of WHO (2004) for drinking water. The groundwater status can be classified as none polluted for PI less than one. However, it can be classified as slightly polluted, moderately polluted, strongly polluted and seriously polluted for PI value ranges 1–2, 2–3, 3–5 and > 5, respectively (Amiri et al. 2015).

The various groundwater chemistry parameters were calculated and categorized to determine the suitability of irrigation groundwater quality based on recommendations for sodium adsorption ratio (SAR) (Richards 1954), sodium percentage (%Na) & combined effects of electrical conductivity of irrigation water (ECiw) with Na% and SAR (Wilcox 1955), Kelly's Ratio (KR) (Nassem et al. 2010), Permeability Index (KI), Magnesium Hazard indices (MH), Residual sodium bicarbonate (RSB) (Ghalib 2017) and Bicarbonate ($HCO_3^-$) hazard (WHO 2004) for irrigation water as given in Eqs. (4–8) bellow when all values of parameter are expressed in meq/L.

$$\%\text{balance error} = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \times 100 \tag{1}$$

$$CaCO_3 = 2.5\left(Ca^{2+}\right) + 4.1\left(Mg^{2+}\right) \tag{2}$$

$$PI = \sqrt{\frac{\left[\left(\frac{C_i}{S_i}\right)_{\text{Max}}^2 + \left(\frac{C_i}{S_i}\right)_{\text{Min}}^2\right]}{2}} \tag{3}$$

$$SAR = Na^+ / \left[\left(Ca^{2+} + Mg^{2+}\right)/2\right]^{1/2} \tag{4}$$

$$\%Na = \left[\left(Na^+ + K^+\right) \times 100\right] / \left(Ca^{2+} + Mg^{2+} + Na^+ + K^+\right) \tag{5}$$

$$KR = Na^+ / \left(Ca^{2+} + Mg^{2+}\right) \tag{6}$$

$$RSB = \left(HCO_3^- - Ca^{2+}\right) \tag{7}$$

$$KI = \left(Na^+ + \sqrt{(HCO3^-)}\right)/\left(Ca^{2+} + Mg^{2+} + Na^+\right) \times 100 \tag{8}$$

$$MH = Mg^{2+}/\left(Ca^{2+} + Mg^{2+}\right) \times 100 \tag{9}$$

The point datasets obtained from field survey and laboratory analysis were transformed into ArcGIS 10.4 platform and raster datasets were used to produce each thematic map using inverse distance weighted interpolation (IDW) method to show the spatial distributions of EC, TDS, TH, PI and major ions. Geospatial distribution analysis tools like inverse distance weighted (IDW) method of interpolation is vital to produce raster surface (Idowu et al. 2017; Gidey 2018). Furthermore, to determine the functional sources of ions and the factors that governing the trends in the hydrochemistry of the watershed, multivariate statistical analysis such as correlation chemical analysis and principal component analysis (PCA) were performed for the water samples.

## Results and discussion

### Physico-chemical and geospatial distribution analyses

The summary of the analytical results and univariate statistical measures of parameter such as minimum, maximum, mean and standard deviation is presented in Table 1.

Based on the water chemistry analysis results, the major cation in the studied groundwater is $Ca^{2+}$, followed by $Mg^{2+}$ and $Na^+$. $HCO_3^-$ is the dominant anion, followed by $SO_4^{2-}$ and $Cl^-$.

The pH of groundwater samples analyzed in the watershed ranges from 6.8 to 8.5, which elaborates a trend from weakly acidic to alkaline chemical reaction within the groundwater system. There is no samples fall above the Compulsory Ethiopia Standard CES (2013) recommended permissible limits for pH.

There is a high variation in electrical conductivity (EC) of groundwater in the watershed ranging from 421 μS cm$^{-1}$ in the close the eastern upper slopes of Gergera mountains i.e. the upper part of the watershed to 1143 μS cm$^{-1}$ in the western aquifer of the watershed i.e. the lower section of the watershed, with a mean of 672 μS cm$^{-1}$. EC was found to be much higher than the permissible limits as prescribed by the WHO standard. Lowest EC is located in the recharge areas originating from spring at the contact point of basement and Adigrat Sandstone, while individual elevated EC values should have variable origins, such as intensive agricultural practices, the shallow depth of water table well and subsequent high evaporation, and geological conditions acquiring high concentration of the dissolved minerals. Hence, Of the 22 samples analysed, 100% have EC values above the WHO maximum permissible limit of 400 μS/cm. Spatial distribution map of the EC is indicated in Fig. 2a. Generally,

**Table 1** The statistical summary of the physico-chemical parameters of Gergera groundwater samples collected from the study area

| Parameters | Max permissible limits | | Range | | | | No. of samples above permissible limits | |
|---|---|---|---|---|---|---|---|---|
| | CES (2013) | WHO (2004) | Min | Max | Mean | Std dev | CES (2013) | WHO (2004) |
| pH | 6.5 – 8.5 | 6.2 – 9.2 | 6.8 | 8.5 | 7.4 | 0.43 | Nil | Nil |
| EC | – | 400 | 421 | 1143 | 672 | 183 | Nil | 22 |
| TDS | 1000 | 1500 | 269 | 732 | 430 | 117 | Nil | Nil |
| $Ca^{2+}$ | 75 | 200 | 54.12 | 108.2 | 83 | 15.97 | 16 | Nil |
| $Mg^{2+}$ | 50 | 150 | 13.20 | 45 | 23.7 | 7.10 | Nil | Nil |
| $Na^+$ | 200 | 200 | 11.50 | 39.7 | 20.10 | 6.56 | Nil | Nil |
| $K^+$ | 1.5 | 12 | 0.00 | 3.30 | 1.20 | 0.90 | 5 | Nil |
| $Fe^{2+}$ | 0.3 | 1.0 | 0.31 | 0.60 | 0.39 | 0.05 | 22 | Nil |
| $HCO_3^-$ | 200 | 380 | 222 | 463 | 324.4 | 64.50 | 22 | 4 |
| $SO_4^{2-}$ | 250 | 400 | 7.92 | 92.40 | 35.10 | 16 | Nil | Nil |
| $Cl^-$ | 250 | 600 | 16.50 | 46.40 | 27.20 | 7.10 | Nil | Nil |
| $NO_3^-$ | 50 | – | 0.15 | 43.60 | 10.30 | 11.70 | Nil | Nil |
| $NO_2^-$ | 50 | | 0.00 | 0.08 | 0.04 | 0.02 | Nil | Nil |
| $F^-$ | 1.5 | 1.5 | 0.00 | 0.80 | 0.37 | 0.16 | Nil | Nil |
| $Br^-$ | | | 0.34 | 1.75 | 0.65 | 0.33 | Nil | Nil |
| $PO_4^{2-}$ | – | – | 0.00 | 0.06 | 0.01 | 0.01 | Nil | Nil |
| $Li^+$ | – | – | 0.00 | 0.01 | 0.003 | 0.01 | Nil | Nil |
| $NH_4^+$ | 1.5 | – | 0.00 | 0.5 | 0.06 | 0.10 | Nil | Nil |

All units are in mg/L except for EC (μS/cm) and pH

EC values increase from recharge areas in eastern towards discharge areas in west of the watershed.

The total dissolved solids (TDS) in the groundwater ranges from 294.7 to 732 mg L$^{-1}$ with a mean of 430 mg/L. 13.6% of the sampled water was found to be much higher than the desirable limits (500 mg/L) as prescribed by the WHO (2004) standard, while 86.4% fall within the desirable limits. However, there was no TDS value that found to be much higher than the maximum permissible limits (1500 mg/L) as prescribed by this WHO standard. The lowest and highest TDS were recorded in the same location where the lowest and highest EC values were recorded. Hence, the possible sources for the higher TDS in the watershed may include dissolved solids from natural sources and agricultural runoff. The geospatial analysis for TDS suggests that the concentration of TDS increases towards the alluvial plain of the watershed (Fig. 2c.).

Among the physico-chemical parameters studied, total iron, potassium and calcium were found to be much higher than the maximum limits as prescribed by the CES (2013) standards. The total hardness (TH) of the watershed varies from 119.30 to 287.30 mg/L, with a mean of 183 mg/L. Of the 22 samples analyzed, the TH classification (Kaur et al. 2017) (Table 2), most groundwater fall within the hard (41%) and very hard (54.5%) class and as such cannot be categorized as drinkable.

The highest value of 287.30 mg/L was recorded at the downstream section of the watershed, due to the highest value 45 mg/L of $Mg^{2+}$ in the groundwater. Whilst the lowest value of 119.30 mg/L recorded at the location of upper-part due to the lowest concentration 13.2 mg/L of $Mg^{2+}$. The spatial distribution analysis for TH explained that the TH increased from the eastern part (upperpart) toward the western part (downward) of the watershed (Fig. 2b).
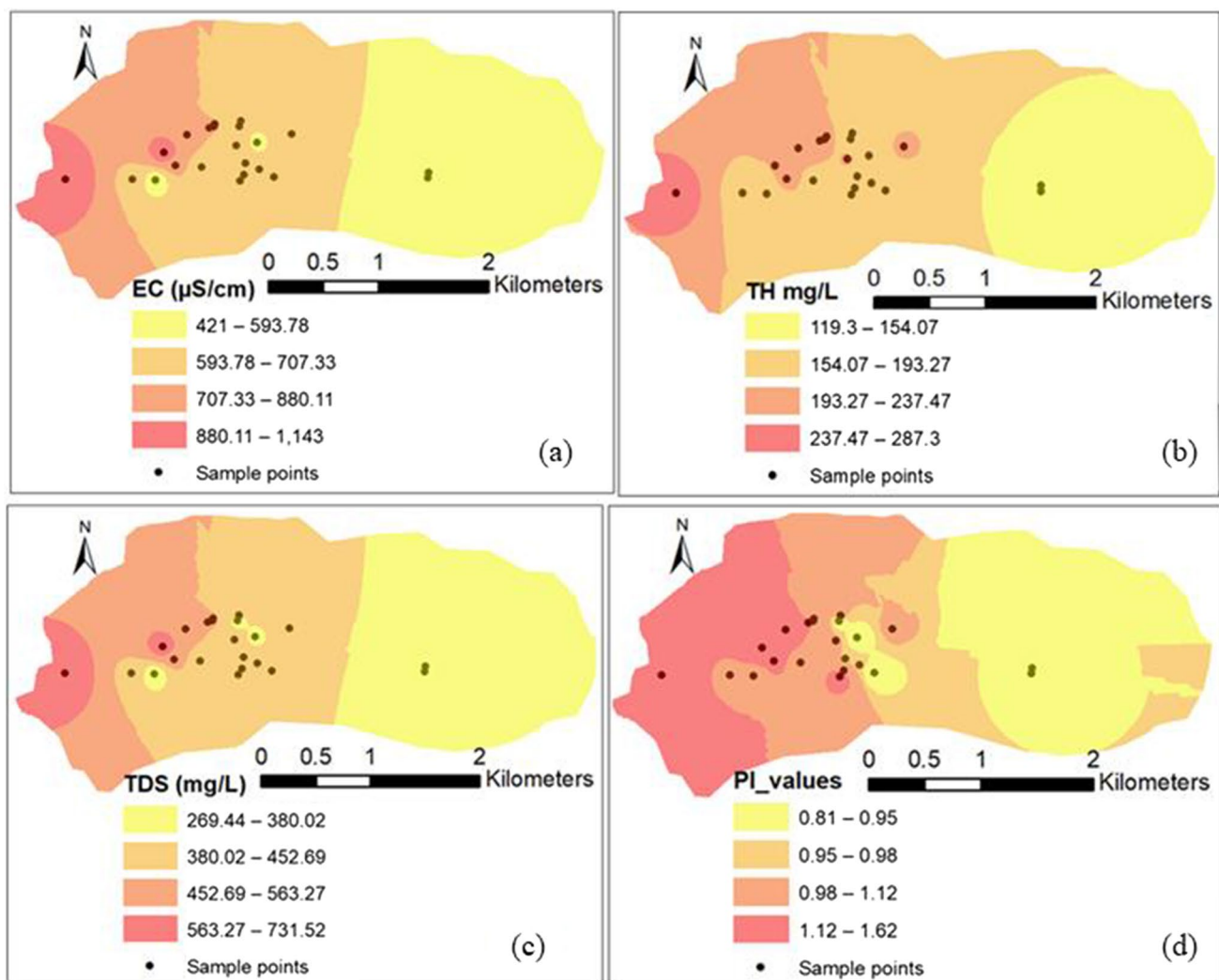


**Fig. 2** Spatial distribution for drinking water quality classification based on weighted overlay model for: **a** EC, **b** total hardness (TH), **c** TDS and **d** pollution index (PI)

**Table 2** Classification of groundwater samples of the study area on the basis of TH and TDS

| Parameters | Range | Water class | No of samples | Percent (%) |
|---|---|---|---|---|
| Total hardness (TH) (mg/L) | $0 - 60$ | Soft | Nil | Nil |
| | $61 - 120$ | Moderately hard | 1 | 4.5 |
| | $121 - 180$ | Hard | 9 | 41 |
| | $> 180$ | Very hard | 12 | 54.5 |
| Total dissolved solids (TDS) (mg/L) | $< 1000$ | None saline | 22 | 100 |
| | $1000 - 3000$ | Slightly saline | Nil | Nil |
| | $3000 - 10{,}000$ | Moderately saline | Nil | Nil |
| | $> 10{,}000$ | Very saline | Nil | Nil |
| Pollution index (PI) | $< 1$ | No pollution | 5 | 22.7 |
| | $1 - 2$ | Slightly polluted | 17 | 77.3 |
| | 2–3 | Moderately polluted | Nil | Nil |
| | 3–5 | Strongly polluted | Nil | Nil |
| | $> 5$ | Seriously polluted | Nil | Nil |

Calcium is the dominant cation in the study area and is largely responsible for the hardness of water. Similar result for calcium dominancy was found in the southern part of the region by Gidey (2018). $Ca^{2+}$ in the study area varies from 45.1 to 108 mg/L, with a mean of 83 mg/L. 73% of the 22 groundwater samples analysed showed $Ca^{2+}$ values exceeding their maximum permissible limit of 75 mg/L (CES 2013) while the 27% fall within the permissible limit of the CES. The high $Ca^{2+}$ and $Mg^{2+}$ values confirm the high total hardness recorded and finally makes the water none potable (unfit for drinking). This hardness of water may be caused due to the calcareous property of soil in the study area.

Magnesium ($Mg^{2+}$) is the dominant ion next to calcium ion in the study area. It varies from 13.20 to 45 mg/L, with a mean of 23.70 mg/L. None of the samples showed magnesium value exceeding their maximum permissible limit of 150 mg/L (CES 2013; WHO 2004). $Mg^{2+}$ typically arises in reduced amount than $Ca^{2+}$ in groundwater due to the fact that the dissolution of $Mg^{2+}$ rich rocks is slow process.

Sodium ion ($Na^+$) and potassium ion ($K^+$) concentrations varies from 11.50 to 39.7 and 0.00 to 3.30 mg/L, with a mean of 20.10 and 1.20 mg/L respectively. $Na^+$ does not have any prescribed limits for drinking water but the high levels of $Na^+$ in drinking water makes it salty in nature (Kaur et al. 2017). Five water samples have $K^+$ values above the CES maximum permissible limit of 1.5 mg/L.

The total iron ($Fe^{2+}$) concentrations in the study area ranges from 0.31 to 0.60 mg/L, with a mean of 0.39 mg/L indicating that all samples were found to exceed the maximum permissible limit of $Fe^{2+}$ for drinking water (0.3 mg/L by CES). Excessive $Fe^{2+}$ may give water a metallic flavour and affect how food and beverages taste. As iron is the second most plentiful metallic element in the Earth's crust (Davison 1993), iron in groundwater might originate from a diversity of mineral sources; and numerous sources of iron might be exist in a single groundwater aquifer system.

Oxidation–reduction reactions, organic matter content, and the metabolic activity of bacteria can influence the concentration of iron in the groundwater (Davison 1993). The highest $Fe^{2+}$ concentration of 0.60 mg/L occurs at the geology of Adigrat sandstone aquifer in the watershed. The existence of Adigrat and Enticho sandstones in the study area are assumed to be the main sources for the distribution of total iron concentrations.

Among the anions concentrations, bicarbonate ($HCO_3^-$) represents the first dominant anion, ranging from 222 to 463 mg/L, with a mean of 324.4 mg/L, followed by $SO_4^{2-}$ and $Cl^-$. The lowest $HCO_3^-$ value of 222 mg/L located at the point of contact spring, while the highest value of 463 mg/L located at the downstream of the watershed. The possible source for the presence of high $HCO_3^-$ in groundwater is the soil, by dissociation of carbonic acid ($H_2CO_3$) produced by the reaction of water with $CO_2$. The decay of organic matter from intensive agricultural activities in the study area can contribute to the enrichment of $CO_2$ in the soil. Further, high $HCO_3^-$ values could have derived from $CO_2$ in the atmosphere and by dissolution of carbonate (dolomite) rocks in the study area. The results of this study are similar to the results reported by Salifu et al. (2017) for the middle voltaian aquifers of the Gushegu district of the northern region of Ghana.

From the pH ranges ($6.8 - 8.2$) in the study area and the carbonic acid dissociation stage in the bicarbonate stage, the important anion is $HCO_3^-$ rather than the $CO_3^{2-}$ in all groundwater samples, bcause all $CO_3^{2-}$ are gone at pH less than or equal to 8.3 (Walton 1970). All the pH values are also greater than 3.82. Therefore, consideration for the concentration of $H^+$ is not important in the ions balance calculation as it is very low. The concentration of $OH^-$ ions in solution is about 7 in the orders of magnitude lower compared to the $H^+$ ions. This is also insignificant to consider in the ionic balance. Hence, the $HCO_3^-$ ion

was expressed in terms of the differences between sum of conservative cations and sum of conservative anions. Generally, out of the 22 samples analysed, 82% fall within the recommended allowable limit of 380 mg/L $HCO_3^-$ in water (WHO 2004), while the remaining 18% fall above the recommended allowable limit.

Sulphate ions ($SO_4^{2-}$) concentration in the watershed varies from 7.92 to 92.40 mg/L, with a mean of 35.10 mg/L. The lowest and highest $SO_4^{2-}$ values are recorded at the downstream and upper stream of the watershed, respectively. It is in the same location where the highest $HCO_3^-$ value was recorded. With respect to the WHO (2004) recommended allowable limit for sulphate in groundwater (200 mg/L), the waters could be safe to be drinkable.

Chloride ($Cl^-$) concentrating in the watershed ranges from 16.50 to 46.40 mg/L, with a mean of 27.20 mg/L. The lowest and highest $Cl^-$ values are recorded at the contact spring (located at the upper part) and at the downstream of the watershed, respectively. The water sample point at the downstream happens to be the same location where the highest $SO_4^{2-}$ value was recorded. None of the samples showed the Chloride concentration above the permissible limit of 250 mg/L by CES (2013).

Nitrate in groundwater generally originates from nitrate sources on the land surface, in the soil zone, or from the applications of nitrogen contained fertilizers (commonly urea, nitrate or ammonium compounds) that are used in agricultural practices (Salifu et al. 2017). Nitrate concentration in the studied watershed ranges from 0.15 to 43.60 mg/L, with a mean of 10.30 mg/L, falling within the CES and WHO guideline limits of 50 and 45 mg/L, respectively.

The fluoride content in the groundwater of the study area ranges from 0.00 to 0.80 mg/L, with mean and standard deviation of 0.37 and 0.16 mg/L, respectively. The fluoride concentrations in the groundwater are below the CES and WHO maximum permissible limit of 1.5 mg/L, which otherwise contributes to tooth caries.

In general, the relative abundance of major cations and anions of the groundwater samples in the study area from the highest to the lowest was $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ & $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$ respectively. The concentration of $NH_4^+$, $NO_2^-$, $Li^+$ and $PO_4^{2-}$ in the groundwater varied from 0 to 0.5, 0 to 0.8, 0.00 to 0.01 and 0 to 0.06, with mean values of 0.06, 0.04, 0.003 and 0.004 mg/L, respectively. All analysed water samples of the studied area have insignificant concentrations of manganese and strontium. Therefore, we did not include the concentrations of manganese and strontium in our statistical summary results. The dissolved oxygen ($O_2$) and temperature (°C) of the groundwater also varied from 0.11 to 8.1 and 19 to 24 with mean value of 3.4 mg/L and 21 °C, respectively. This reflects generally more anoxic conditions rather than oxic and therefore favors more reduction to oxidation.

The spatial distribution map of major cations and anions, except $K^+$ and $NO_3^-$, in Gergera watershed showed that the major cations and anions concentration distribution increased from the eastern part (upperpart) toward the western part (downward) of the watershed (Figs. 3 and 4), suggesting that the sources of major cations and anions in groundwater are rock weathering and anthropogenic pollution sources including runoff and drainage from irrigable agricultural practices in the study area.

The spatial distribution map of $K^+$ in the watershed showed that the $K^+$ concentration increased from the downward toward the upperpart of the watershed (Fig. 3d), especially around the deep drilled aquifer materials, indicating that the important source of $K^+$ in groundwater is dissolution of potassium-bearing minerals such as sylvite (KCl), Jarosite-K, potash contained fertilizers and as well as due to use of runoff water for irrigation. Potassium is generally more easily fixed on clay minerals in the rock matrix. Hence it is the least abundant among the major cations.

The spatial distribution map of $NO_3^-$ showed that its concentration distribution increased from all directions concentrating towards the central part of the watershed, especially around the highly extracted wells, were high concentrations of $NO_3^-$ distribution (Fig. 4d). This indicates that the main sources of $NO_3^-$ could be derived from return flow during water fetch, infiltration of local sewage, animal excrement, runoff and drainage from irrigable agricultural lands as also described in Salifu et al. (2017) and Kasper et al. (2019).

## Pollution index (PI)

The groundwater quality was assessed using pollution index (PI) and the results revealed that 55% of the water samples showed PI above 1 indicating that most groundwater in the study area are slightly polluted while 45% of the water samples were none polluted (Table 2). The spatial distribution of PI for overall quality of water result using rating the combined influence of each parameter method is classified based on weighted overlay model. The final spatial distribution analysis of PI method result showed that PI severity increased toward the downstream of the watershed (Fig. 2d). The increased levels of PI towards the downstream might be due to the presence of natural and human influence directing towards the downstream by the present effects of leaching and runoff in the watershed. This finding is in line with Amir et al. (2015) who suggested that the groundwater quality becomes significantly worsened towards the downstream of the area following the groundwater flow paths.
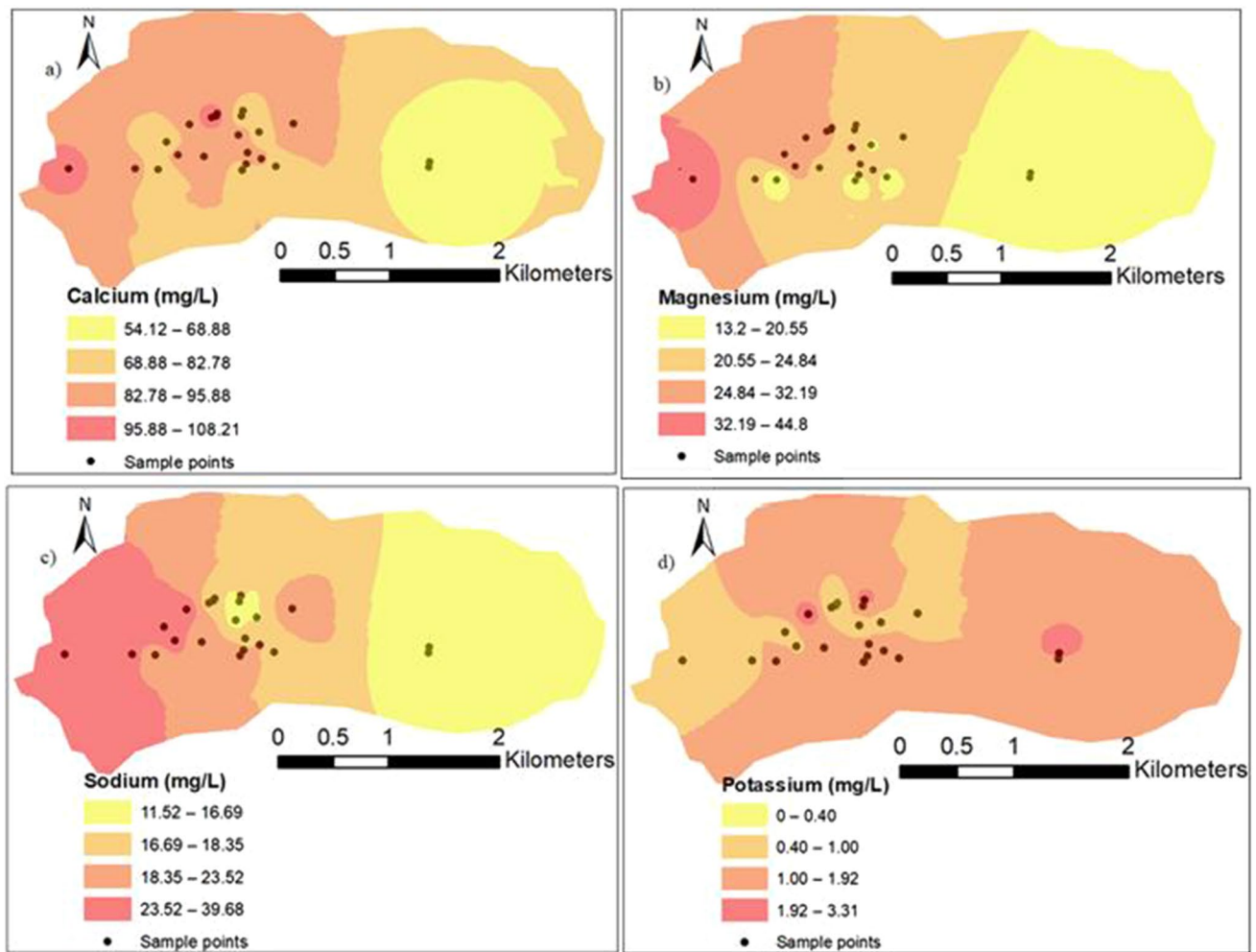
**Fig. 3** Spatial distribution for major cations classification based on weighted overlay model

## Multivariate statistical analysis of groundwater chemical

To understand the natural and anthropogenic influences on groundwater as well as to facilitate solution for such problems, multivariate statistical techniques play a great role in our ecosystem (Selvakumar et al. 2017; Dişli and Gülyüz 2020). Correlation analysis and principal component analysis (PCA) have been widely used as unbiased approaches in the study of groundwater quality data for obtaining meaningful information (Ravikumar and Somashekar 2010).

### Correlation analysis

The correlation analysis is a method to evaluate the relationships between physico-chemical properties of groundwater which can reveal the major hydrochemical evolution processes within an aquifer and can also be used to deduce the sources of ions and the origin of the groundwater

(Jothivenkatachalam et al. 2010; Wu et al. 2013). The strong or moderate positive relations are pointers of the importance of the parameters in the groundwater hydrochemistry of the study area and their trend to follow similar propensity (Gidey 2018). The correlation matrices test for 14 water quality parameters of 22 groundwater samples were calculated using PAST software and the values of the correlation coefficient are given in Table 3.

EC and TDS have a high correlation ($r = 1$) to each other suggesting an absolute straight linear association. Table 3 shows that $Mg^{2+}$, $Br^-$, $Na^+$, $Cl^-$, $HCO_3^-$, and $SO_4^{2-}$ are strongly correlated with TDS with the r value of 0.91, 0.89, 0.83, 0.70, 0.67 and 0.6, respectively, which indicate that these ions are the most effective in the mineralization and salinization of the groundwater of the watershed. Their concentrations also mostly influenced from the sources of geological and chemicals used in agriculture and domestic discharges that increase towards the downstream of the watershed due to the effect by runoff. $Br^-$ concentration is
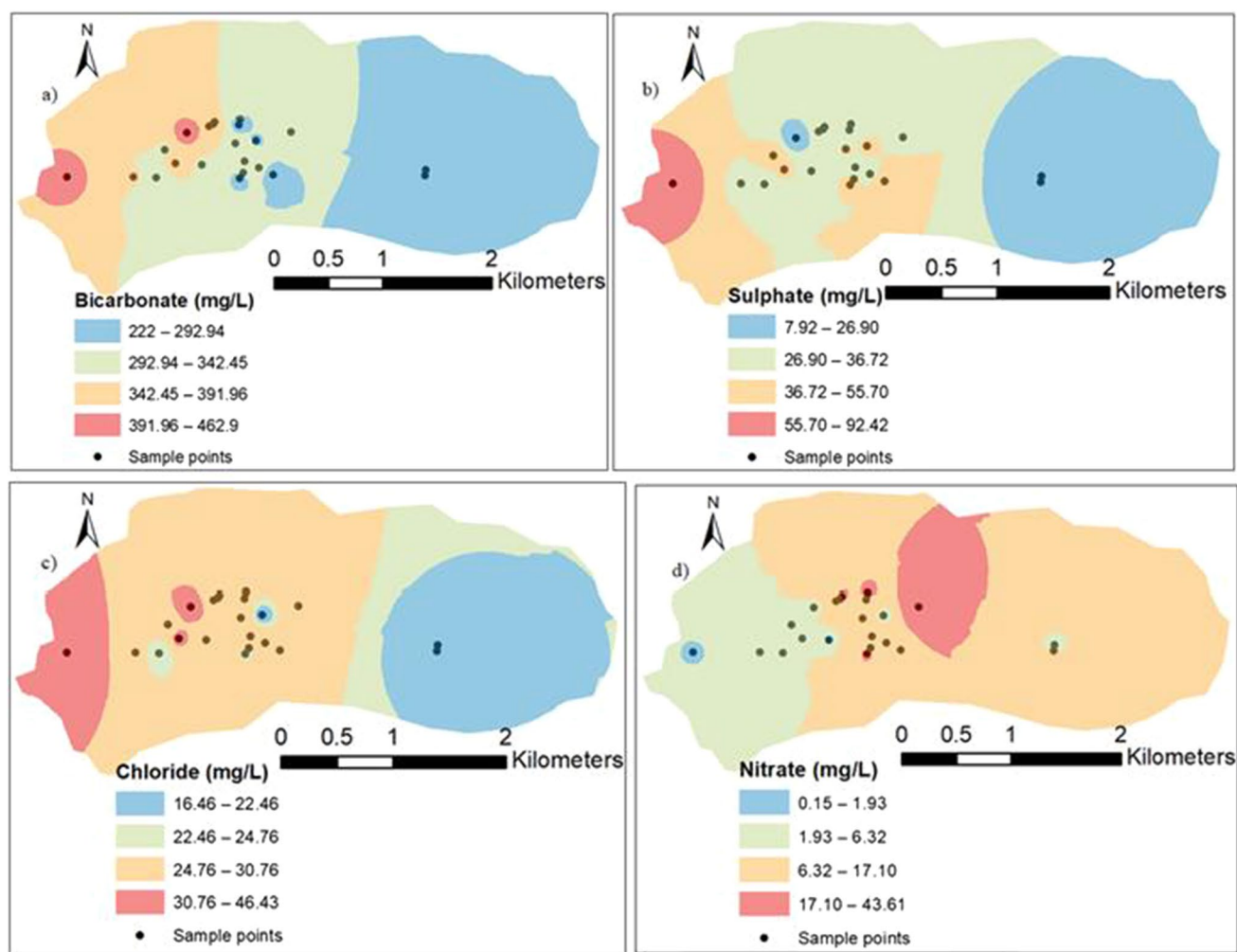
**Fig. 4** Spatial distribution for major anions classification based on weighted overlay model

**Table 3** Pearson correlation coefficients for 14 hydrogeochemical parameters of groundwater samples of Gergera watershed

|  | F⁻ | Cl⁻ | Br⁻ | NO₃⁻ | SO₄²⁻ | Ca²⁺ | Na⁺ | K⁺ | Mg²⁺ | HCO₃⁻ | EC | TDS | TH | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| F⁻ | 1 |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Cl⁻ | −0.14 | 1 |  |  |  |  |  |  |  |  |  |  |  |  |
| Br⁻ | −0.05 | **0.68** | 1 |  |  |  |  |  |  |  |  |  |  |  |
| NO₃⁻ | −0.24 | 0.11 | −0.14 | 1 |  |  |  |  |  |  |  |  |  |  |
| SO₄²⁺ | −0.19 | 0.46 | **0.71** | −0.06 | 1 |  |  |  |  |  |  |  |  |  |
| Ca²⁺ | −0.10 | **0.69** | 0.35 | 0.22 | 0.25 | 1 |  |  |  |  |  |  |  |  |
| Na²⁺ | 0.42 | **0.53** | **0.63**\*\* | −0.12 | 0.40 | 0.10 | 1 |  |  |  |  |  |  |  |
| K⁺ | −0.07 | −0.03 | −0.26 | −0.10 | −0.43 | −0.32 | −0.06 | 1 |  |  |  |  |  |  |
| Mg²⁺ | 0.02 | **0.85** | **0.84** | −0.11 | **0.57** | **0.52** | **0.69** | −0.22 | 1 |  |  |  |  |  |
| HCO₃⁻ | 0.17 | **0.78** | **0.57** | −0.10 | 0.20 | **0.82** | **0.52** | −0.20 | **0.81** | 1 |  |  |  |  |
| EC | 0.21 | **0.70** | **0.89** | −0.02 | **0.65** | 0.38 | **0.83** | −0.31 | **0.91** | 0.67 | 1 |  |  |  |
| TDS | 0.21 | **0.70** | **0.89** | −0.02 | **0.65** | 0.38 | **0.83** | −0.32 | **0.91** | 0.67 | 1 | 1 |  |  |
| TH | −0.03 | **0.90** | **0.76** | 0.01 | **0.51** | **0.78** | **0.55** | −0.29 | **0.94** | **0.92** | 0.82 | 0.82 | 1 |  |
| pH | −0.26 | 0.10 | 0.09 | −0.26 | 0.05 | −0.35 | 0.11 | 0.28 | 0.11 | −0.15 | 0.02 | 0.02 | −0.06 | 1 |

Coefficients are significant at the 0.05 level and those higher or equal to 0.50 were shown as bold fonts

closely correlated with $Cl^-$ suggesting that both $Br^-$ and $Cl^-$ have a common source (salt). There is an increase in $Br^-/Cl^-$ ratio along the downstream due to the dissolution of halite from one or more sources. In addition to this, there is also a predictable correlation between $Br^-$ and EC indicating more than one main source of salts contributes to the noticed conductivity. There is a gradual increase in $Br^-$ levels as distance from the upper watershed increase following the direction of groundwater streamlines. This is caused by the dissolution, runoff and leaching of ions out of soil. The increase in concentration follows the same pattern for the other ions too. The moderate correlation between $Na^+$ and $Cl^-$ ($r = 0.53$) indicates that the major sources of these elements were influenced by marine deposits and dissolution of halite during groundwater flow.

The concentration of $Ca^{2+}$ and $Mg^{2+}$ have a strong positive correlation with TH ($r = 0.78$ and $0.94$, respectively), which is emphasize as hardness is mainly measure of $Ca^{2+}$ and $Mg^{2+}$. The strong correlation of $Ca^{2+}$ and $Mg^{2+}$ with TH indicates that $Ca^{2+}$ and $Mg^{2+}$ control the alkalinity character of the groundwater. TH is also strongly correlated with $HCO_3^-$ ($r = 0.92$) and moderately correlated with $SO_4^{2-}$ ($r = 0.51$), suggesting that TH is basically a temporary hardness. There is a weak correlation of $Ca^{2+}$ with $SO_4^{2-}$ ($r = 0.25$) but a strong correlation of $Na^+$ with $Mg^{2+}$ ($r = 0.69$), implying that the dissolution of gypsum or anhydrite alone may not be expected as a main sources of $Ca^{2+}$ and $SO_4^{2-}$. Other reactions involving $Ca^{2+}$, such as dolomite or calcite dissolution/precipitation and ions exchange, may well account for the correlation with $SO_4^{2-}$. For example, $HCO_3^-$ has a similar and strong correlation with both $Ca^{2+}$ ($r = 0.82$) and $Mg^{2+}$ ($r = 0.81$), so the dissolution of dolomite can be assumed as a main source of $Ca^{2+}$, $Mg^{2+}$ and $HCO_3^-$. $K^+$, $NO_3^-$, $F^-$ and pH did not show any correlation with almost all parameters. Hence, the main parameters controlling the groundwater hydrogeochemistry are TDS, EC, TH, $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $HCO_3^-$, $SO_4^{2-}$ $Cl^-$ and $Br^-$ whilst changes in $K^+$, $NO_3^-$, $F^-$ and pH have minimal influences in the hydrogeochemistry of the study area.

## Principal component and factor analysis

Principal component analysis (PCA) is a method for pattern recognition that attempts to describe the alteration of a large set of inter-correlated variable (Ravikumar and Somashekar 2017). PCA extracts associations and enables to reduce the number of dataset into components that describe a portion of the total variance between groundwater's chemical parameter. An eigenvalue provides a measure of the significance factor, where the uppermost eigenvalue resembles the greatest important. Eigenvalues > 1 are considered significance. Table 4 presents the PCA results comprising the loadings, Eigenvalues, percentage of total and cumulative variance for

**Table 4** Factor loadings for 15 hydrochemical parameters of groundwater

| Variables | PC1 | PC2 | PC3 | PC4 | PC5 |
|---|---|---|---|---|---|
| Mg | **0.96** | 0.10 | 0.03 | −0.16 | 0.02 |
| TH | **0.95** | −0.20 | −0.04 | −0.20 | 0.04 |
| TDS | **0.95** | 0.19 | 0.03 | 0.23 | 0.00 |
| EC | **0.95** | 0.19 | 0.03 | 0.23 | 0.00 |
| $Cl^-$ | **0.85** | −0.17 | 0.20 | −0.24 | 0.26 |
| $Br^-$ | **0.88** | 0.18 | 0.22 | 0.09 | −0.13 |
| $HCO_3^-$ | **0.83** | −0.23 | −0.32 | −0.27 | 0.22 |
| Na | **0.73** | 0.45 | −0.10 | 0.29 | 0.25 |
| Ca | **0.62** | **−0.68** | −0.15 | −0.22 | 0.07 |
| $SO_4^{2-}$ | **0.64** | 0.09 | 0.37 | 0.20 | **−0.50** |
| $NO_3^-$ | −0.04 | **−0.64** | 0.35 | 0.37 | 0.22 |
| pH | −0.01 | **0.60** | 0.47 | −0.45 | 0.02 |
| $F^-$ | 0.09 | 0.33 | **−0.76** | 0.41 | 0.23 |
| K | −0.33 | 0.30 | 0.21 | −0.30 | **0.73** |
| $Fe^{2+}$ | −0.10 | −0.13 | **0.51** | **0.60** | 0.40 |
| % of variance explained | 48.4 | 12.6 | 10.6 | 9.6 | 8.3 |
| %cumulative variance | 48.4 | 61 | 71.6 | 81.2 | 89.5 |

*Samples*: coefficients are significant at the 0.05 level and those higher or equal to 0.50 were shown as bold fonts
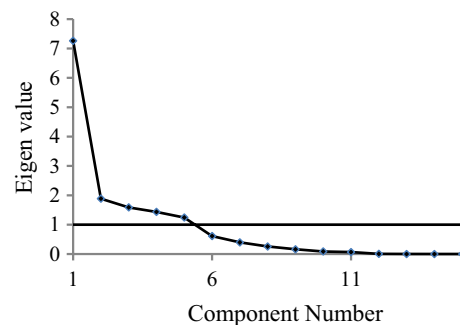


**Fig. 5** PCA scree plot of the Eigenvalues for the dataset of groundwater samples

chemical parameter on five significant principal components (PCs).

Based on the criteria of Cattell and Jaspers (1967), five principal components (PCs) with Eigenvalues > 1 were taken. The five factors (PCs) explain 89.5% of the total variance of the groundwater dataset, are responsible for governing geochemistry of groundwater in the study area. The scree plot indicated in Fig. 5 is also the method of identifying a number of useful PCs, in which, a sharp decline in sizes of Eigenvalues where results in an alteration in the slope of the plot from steep to shallow could be detected.

The clarified variance is mostly associated to the chemical parameters loadings are categorized as 'strong' (>0.70), 'moderate' (0.70–0.50) and 'weak (0.50–0.30) (Liu et al.

2003). PC1, which explained 48.4% of the total variance, had strong and moderate positive loadings particularly with $Mg^{2+}$, TH, TDS, EC, $Br^-$, $Cl^-$, $HCO_3^-$, $Na^+$, $SO^{2-}$ and $Ca^{2+}$ respectively. Those parameters contribute a significant factor loading could possibly control the groundwater chemistry. High positive loading of $Mg^{2+}$, TH, TDS, EC, $Br^-$, $Cl^-$, $HCO_3^-$, $Na^+$ and moderate loading values for $Ca^{2+}$ and $SO^{2-}$ demonstrate incidence of rock weathering and anthropogenic activities such as irrigation, fertilizer application, waste disposal, excrements from human and livestock, and groundwater abstraction. Hence, PC1 strongly supported for the ideas that described in correlation analysis. The PC2 explains 12.6% of the total variance and has high loadings of pH (positive), $Ca^{2+}$ (negative) and $NO_3^-$ (negative) and are shown on this factor, suggesting that anthropogenic activities (example, $Ca^{2+}$ from use of fertilizers) may have impact on the groundwater chemistry. The sources of $NO_3^-$ could be derived from infiltration of local sewage, animal excrement, runoff and drainage from irrigable agricultural lands.

PC3 explains for 10.6% of the variability and is highly (negative) and moderately (positive) correlated with $F^-$ and Fe respectively. Unlike the concentrations and ratio for $Cl^-$ and $Br^-$ which are related to inputs, the concentrations of $F^-$ and $Fe^{2+}$ together with PC3 result suggest that the principal contribution is by water-acidic rock interaction. PC4 explains for 9.6% of the variability and is highly correlated with Fe and other parameters have been low negative and positive values of loadings. From PC4 loading factor results and geology of the study area, we can infer that the presence of high iron concentrations in groundwater with low sulphate levels may reflect siderite ($FeCO_3$) and Melanterite ($FeSO_4$:$7H_2O$) dissolutions in the aquifer system (Chou et al. 2002). PC5 explains 8.3% of the total variance and has high positive factor loading for potassium and moderate negative loading factor for $SO_4^{2-}$. This can be attributed by weathering of potash silicate minerals, potash fertilizers, drainage and dissolution of secondary salts in the soil together with the agricultural wastes in the watershed. The dissolution of reactive minerals such as Sylvite (KCl) could play a great role to increase the concentration of $K^+$ in the groundwater.

## Water quality classification for irrigation purpose

The chemistry of groundwater is an important consideration in any evaluation of its suitability for irrigation as the groundwater is being used for irrigation in Tigray region. The important water chemistry parameters to understand the quality of water for irrigation purpose include salinity of irrigation water (ECiw), Sodium absorption ratio (SAR), sodium percentage (%Na), bicarbonate ($HCO_3^-$) hazard, residual sodium bicarbonate (RSC), Kelly's ratio (KR),

permeability index (KI) and magnesium hazard (MH) as described in the methodology section.

## Total dissolved solids and ECiw

Integrated quality management of these water quality parameters with soil can prompt maximum crop yield (Gidey 2018). Based on total dissolved solids (TDS) classification, groundwater samples fall in none saline category (Table 2). Considering the salinity of irrigation water (ECiw) for salinity classification, it was found that water samples were categorized under none (63.6%) and slight to moderate (36.4%) salinity degree of restriction classes (Table 5). Therefore, ECiw values indicate presence of two types of groundwater: 1) groundwater that is not hazardous and needs no restriction on use, and 2) groundwater that needs slight to moderate degree of restriction on use.

The first type groundwater can be used for irrigation for almost all crops and for almost all kinds of soils. Very small salinity level might grow which might need slight supervision; however it is allowable under usual irrigation performs except in soils of very low permeability. To attain an optimum yield of agriculture using the second category, constant water quality checking program and improvement of management practices such as selection of crop and management alternatives are essential.

## Sodium absorption ratio (SAR)

SAR is an important parameter to evaluate the suitability of water for irrigation purposes, because sodium concentration can decrease the soil penetrability and soil structure (Todd 2005). The SAR values of groundwater varied between 0.76 and 2.86 meq/L with an average value of 1.54 meq/L. The classification of water samples from the study area with respect to SAR (Richards 1954), all the samples were under the excellent category (< 10 meq/L). Therefore, the SAR values revealed that the water is suitable for irrigation.

## Combined effect of SAR with ECiw

The classification of water samples using the combined effect of sodium absorption ratio with salinity of irrigation water (SAR-ECiw) (Wilcox 1955) indicated that 36.4% of water samples have no hazards of sodicity will arise if the groundwater from these wells is considered for use. While the remaining (63.6%) of the samples suggest that the water from these wells need slight to moderate degree of restriction on use (Table 5). If appropriate managements are not implemented, those groundwater which have slight to moderate restriction on use currently can attain severe restriction on use and sodium toxicity for future surface irrigation will happened. The irrigation water with $HCO_3^-$ in high pH

**Table 5** Water quality and its potential irrigation problems

| Indices for water quality | Degree of restriction on use and/or suitability of water for irrigation | | | |
|---|---|---|---|---|
| | | Range | No. of samples | % |
| ECiw (dS/m) | None | < 0.7 | 14 | 63.6 |
| | Slight to moderate | 0.7–3.0 | 8 | 36.4 |
| | Severe | > 3.0 | – | – |
| SAR-ECiw (SAR 0−3) | None | > 0.7 | 8 | 36.4 |
| | Slight to moderate | 0.7–0.2 | 14 | 63.6 |
| | Severe | < 0.2 | – | – |
| RSB (meq/L) | Satisfactory | < 5 | 22 | 100 |
| | Marginal | 5–10 | – | – |
| | Unsatisfactory | > 10 | – | – |
| $HCO_3^-$ (mg/L) | None | < 92 (< 1.5 meq/L) | – | – |
| | Slight to moderate | 92–519 | 22 | 100 |
| | Severe | > 519 | – | – |
| KR | Suitable | < 1 | 22 | 100 |
| | Doubtful | 1–3 | – | – |
| | Unsuitable | > 3 | – | – |
| KI (%) | Unsuitable | < 25 | – | – |
| | Good | 25–75 | 22 | 100 |
| | Excellent | > 75 | – | – |
| MH (%) | Suitable | < 50 | 22 | 100 |
| | Unsuitable | > 50 | – | – |

irrigation water can worsen the soil $Na^+$ hazard by causing $Ca^{2+}$ and $Mg^{2+}$ to precipitate, thereby becoming unavailable to counteract the negative effect of $Na^+$.

### Sodium percentage (%Na) and ECiw-%Na

Sodium percentage is an essential parameter for evaluating sodium hazard and is, therefore, widely used for assessing the suitability of water quality for irrigation usage (Wilcox 1955). The presence of sodium may react with soil, thereby reducing its permeability. The %Na of groundwater ranged from 8.74 to 23.93 with mean value of 13%. The results based %Na (Wilcox 1955), showed that (except one sample, %Na = 23.93, classed as good), all of the samples were found to be excellent category (%Na < 20) for irrigation. However, classification of groundwater samples based on combined effects electrical conductivity of irrigation water or salinity and percent sodium (ECiw-%Na) (Wilcox 1955), showed that 86.4 and 13.6% of the samples found under excellent to good and good to permissible categories respectively. The existence of excess of sodium causes some of the water samples to be in the good-to-permissible ranges and may affects air and water circulation in the soil during wet situation (Ghalib 2017). This result is similar with previous results of Gidey (2018) who reported the salinity hazard results raged from good to permissible water classes for irrigation in surrounding the Mekelle city.

### Residual sodium bicarbonate (RSB)

The irrigation water classification on the basis of RSB was calculated for each groundwater by equation given by Ghalib (2017). The calculated RSB of the groundwater ranged from − 2.8 to − 0.26, with an average value of − 1.18 meq/L. Based on RSB values, all groundwater samples analysed were obtained to be satisfactory (< 5 meq/L) (Table 5), indicating that every groundwater is safe for irrigation purposes.

### Bicarbonate ($HCO_3^-$) hazard

Bicarbonate is another alternative measure of the $Na^+$ content in relative with magnesium and calcium. Bicarbonate ion ($HCO_3^-$) combined with $Ca^{2+}$ or $Mg^{2+}$ may precipitate as $CaCO_3$ or $MgCO_3$ when the soil solution concentrates in drying circumstances. In these circumstances, the concentration of $Ca^{2+}$ and $Mg^{2+}$ could decrease relating to $Na^+$ causing that the SAR value to be bigger, leading the soil to be more alkaline with high pH value. The bicarbonate of the groundwater ranged from 222 to 463 mg/L with an average value of 324.4 mg/L (Table 2). According to $HCO_3^-$ values, all groundwater samples suggest that the water from these wells need slight to moderate degree of restriction on use (Table 5). This study is similar to that of Kawo and Karuppannan (2018) who reported $HCO_3^-$ as a dominant anion of

groundwater in Modjo River Basin found at the central part of Ethiopia.

## Permeability index (KI)

According to KI indices, the groundwater can be divided into excellent, good and unsuitable with values > 75, 25 − 75 and < 25% permeability, respectively (Doneen 1962). Hence, the water quality based on KI showed that all the samples fall in the good quality category ranging from 39.14 to 56.10%, indicating that the waters are suitable for irrigation purpose.

## Magnesium hazard (MH)

The magnesium hazard value is the excess of $Mg^{2+}$ over $Ca^{2+}$ and $Mg^2$. Generally, $Ca^{2+}$ and $Mg^{2+}$ sustain a state of equilibrium in groundwater. However, an excess of magnesium present in water disturbs the soil quality, resulting in poor crop yield returns. This was assessed by calculating MH and the result for all groundwater samples fall in the ranges of 23.8 to 49.8% which are less than 50%, indicating that all the waters are suitable for irrigation purposes (Table 5).

## Kelly's ratio (KR)

KR is one of the important ratios in the assessment of water quality for irrigation purpose (Nassem et al. 2010). A KR of more than one indicates an excess of sodium in waters. Therefore, water with the KR less than one is suitable for irrigation, while those with a ratio more than three are unsuitable for agricultural purpose due to alkali hazards. KR of groundwater of the study area varies from 0.10 to 0.31 (with mean = 0.14) that make all the waters to be in the category of suitable for irrigation purposes (Table 5). Generally, the water with potential problems on use for irrigation concentrates in the western part of the study area.

## Water types in the study area

In this study, major cations and anions ($Ca^{2+}$, $Mg^{2+}$, $Na^+$, $K^+$, $HCO_3^-$, $SO_4^{2-}$ and $Cl^-$) were plotted in a Piper diagram (Piper 1944) to understand the major hydrochemical facies (Fig. 6) using AquaChem v 3.7 Software.

The results of groundwater hydrochemical analysis revealed that majority of the samples belong to Ca–Mg–HCO3 type while the other samples belong to Ca–HCO3 and Ca–Mg–Na–HCO3 type. Based on Walton (1970) method of hydrochemical facies classification, the groundwater samples belonged to temporary hard
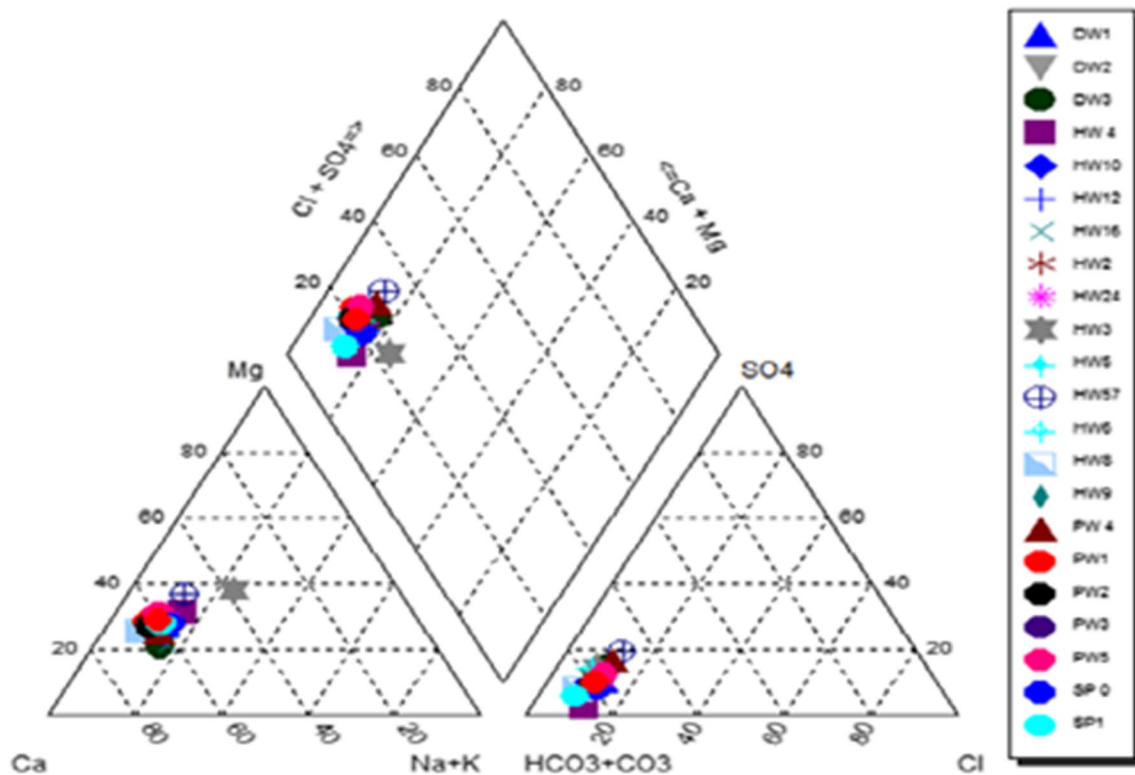


**Fig. 6** Piper diagram showing distribution and classification of water types based on major ions
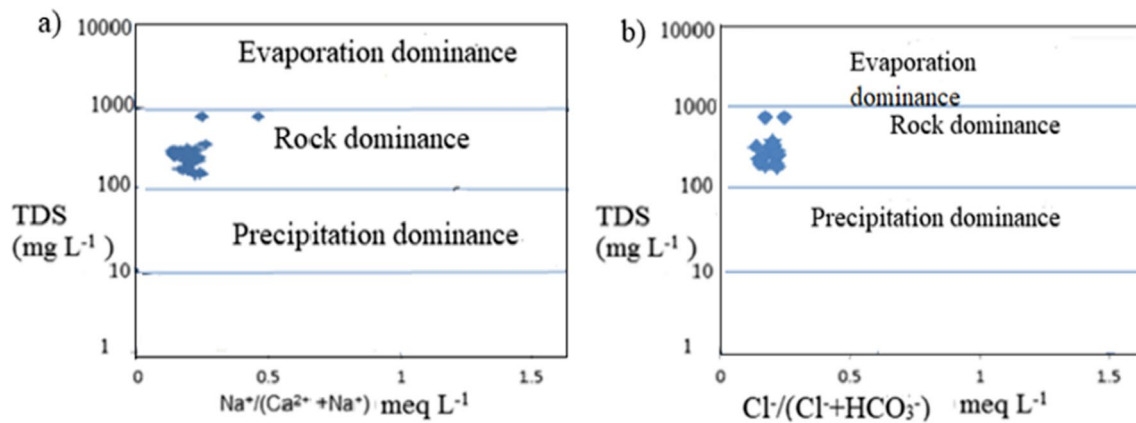
**Fig. 7** Gibbs plot for mechanism controlling groundwater chemistry; **a** Gibbs cations ratio and **b** Gibbs anions ratio

water. This reflected by more than 50% of the total dissolved constituent load in meq/L which is contributed by combined $Ca^{2+}$, $Mg^{2+}$ and $HCO_3^-$. Therefore, recharging characteristics were observed in almost all samples falling in Ca–Mg–$HCO_3$ type; and such waters could considered as dominated in Precambrian aquifer or in unconsolidated deposits containing abundant carbonate minerals. Recharging waters are formed when water infiltrates into the ground from the surface, it carries dissolved carbonate in the form of $HCO_3^-$ and the geochemically mobile $Ca^{2+}$ (Ravikumar and Somashekar 2017). On the basis of this diagram (Fig. 6), it is clear that in all the waters, alkaline earths ($Ca^{2+} + Mg^{2+}$) are higher than alkali element ($Na^+ + K^+$) either due to the preferential release of $Ca^{2+}$ and $Mg^{2+}$ from mineral weathering of exposed bedrock or probably reverse cation exchange reactions of $Ca^{2+} + Mg^{2+}$ into solution and following adsorption of sodium onto aquifer materials.

## Factors controlling groundwater chemistry

Chemistry of groundwater is mainly controlled by the interaction of groundwater with aquifer minerals. The role of rock-water interaction and anthropogenic effects on groundwater can be investigated by diverse hydrogeochemical processes (Kaur et al. 2017). To obtain a highlight into hydrogeochemical processes, Gibbs (1970) has suggested scatter plot method, by using TDS versus $Na^+/(Ca^{2+} + Na+)$ for cations and $Cl^-/(Cl^- + HCO_3^-)$ for anions, illustrating three significant natural mechanism controlling major ion chemistry of the groundwater including the rainfall dominance, water–rock interaction dominance, evaporation and precipitation dominance. It was found that all of the water samples collected from shallow and deep wells falls in rock dominance. This revealed the importance of water–rock interactions as the primary sources of dissolved ions controlling the chemical composition of these waters (Kaur et al. 2017).

This study is similar to that of Li et al (2016) who reported chemical weathering of minerals as main factor controlling the evolution of groundwater chemistry in and around Hua Country (China) (Fig 7).

## Conclusions

Groundwater in the eastern part of Tigray region (Ethiopia) is mainly slightly alkaline freshwater. The abundance of major cations is in the order $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ and that for anions is $HCO^{3-} > SO_4^{2-} > Cl^- > NO_3^-$, which makes the majority of the water samples fall in the class of Ca–Mg–$HCO_3$ water type.

The interpretation of other physico-chemical parameters of groundwater in the study area suggest that they are generally not potable (contaminated) due to their excessive EC, $Fe^{2+}$, TH, PI, $Ca^{2+}$ and $HCO_3^-$ values. The total iron concentration and salinity levels of all water samples found to be beyond maximum permissible limits as prescribed by WHO and CES standards for drinking water. Calcium contents in majority of water samples, as well as potassium and bicarbonate contents in some water samples, were also found to be above maximum permissible limits as prescribed by both standards for drinking water. Based on the pollution index (PI) results, the majority (77.3%) of water samples were found to be slightly polluted. Water samples from majority of the sites were classified as very hard which reveals its unsuitability for drinking purpose. Groundwater in almost all locations have been found to contain < 0.6 mg/L of fluoride thus making those areas susceptible to dental caries, especially in child. Spatial distribution of EC, TH, TDS, PI and major ions display large variations and mostly increased in north-western and western part of the study area. The Pearson correlation analysis results demonstrate that $Mg^{2+}$, $Ca^{2+}$, $Br^-$, $Na^+$, $Cl^-$, $HCO_3^-$, and $SO_4^{2-}$ are strongly correlated

with TH, EC, and TDS, which indicate that these ions are the most effective in the mineralization and salinization of the groundwater in the study area. PCA analysis established that water chemistry parameters under PC1 and PC2 (viz., 48.4 and 12.6% of entire variance) having strong loading was largely considered to control the groundwater chemistry in the study area. According to Gibbs (1970) plot, all groundwater samples fall in rock dominance zone demonstrating that the decomposition of rock plays an important role in controlling the overall chemistry of groundwater.

Regarding the classification of irrigation water according to SAR, %Na, KR, and MH values, all the water samples analysed were found to be suitable for irrigation purposes. According to KI and RSB values, all the water samples are good and satisfactory for irrigation purposes, respectively. However, analysis of the values of ECiw, integrated with SAR (ECiw-SAR values $0-3$) & ECiw-%Na, and $HCO_3^-$ revealed that most samples are not suitable for irrigation purposes which need from slight to moderate degree of restriction on use for irrigation. Hence, most groundwater samples have marginal salinity level which requires a care in selection of crop and management alternatives to achieve a full yield potential. From this study, it is concluded that groundwater in the study district is chemically unfit for drinking and irrigation uses, which needs affirmative solutions such as continuous (at least once per season) water quality monitoring program and a comprehensive hydrochemical study is recommended for future sustainable use of groundwater resources not only in the study district, but in the whole area of Ethiopia.

## Declarations

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