

Ethiopian Journal of Water Science and Technology (EJWST)

Available online at: <u>https://survey.amu.edu.et/ojs/index.php/EJWST</u>

Vol. 4 , 2021, pages: 62~89

ISSN(Print): 2220-7643

Shallow Groundwater Quality and Human Health Risk Assessment in Holte, a Town in Southern Ethiopia

Demamu Tagele Haligamo¹ and Tamru Tesseme Aragaw¹

¹Faculty of Water Supply and Environmental Engineering, Arba Minch Water Technology Institute, Arba Minch University, Arba Minch City, Ethiopia Correspondence to <u>tamruiit@gmail.com</u>

ABSTRACT

Groundwater quality and human health risk assessment are critical for the long-term usage of household water supplies. The purpose of this study was to evaluate groundwater quality and human health risk in Holte, a town in the Derashe Special Woreda in southern Ethiopia. Water samples from seven shallow groundwater wells were taken and examined for hydrogeochemical properties. The Water Quality Index (WQI) was developed to assess the suitability of groundwater for drinking. Groundwater hydrochemistry types and evolutionary processes were investigated. The results suggested that the typical pH of groundwater samples had an average pH of 7.99. The values of electrical conductivity (EC), bicarbonate (HCO3) and total dissolved solid (TDS) in all samples were above the recommended upper limit of World Health Organization (WHO) for drinking water. Based on the hydrochemical findings, the orders of cationic abundance and anionic abundance in the groundwater were $Ca^{2^+} < Mg^{2^+} < K^+ < Na^+$ and $F^- < SO_4^{2^-} < Cl^-$ < HCO₃⁻, respectively. According to the Piper Tri-linear Diagram, the majority of groundwater samples were found to have Mixed Ca-Na-HCO3. The Gibbs fields results showed that evaporation dominated groundwater quality, whereas chemical weathering of rock-forming minerals dominated the remaining samples. The calculated WQI result showed that 57.1% (4 handpumps) of groundwater samples from the town had acceptable water quality, but 42.9% (3 handpumps) had poor water quality. The finding of this study suggests that groundwater quality parameters should be tested and monitored on handpumps at sample locations 1, 2, and 3 in the town to minimize human health risks and ensure long-term socioeconomic development.

Keywords: Shallow Groundwater Quality, Water Quality Index, Health Risk Assessment, Hydrochemistry

Received: 17 October 2022 accepted 18 Nov 2022.

1. INTRODUCTION

Groundwater (GW) has an essential role in maintaining social and economic development of humankinds. The needs for two-third of the world's population will be fulfilled by groundwater alone (Adimalla et al. 2020). It is a primary source for domestic use in many rural areas of the world including developing countries (Alam et al. 2020; Lapworth et al. 2017). In India, the annually used groundwater is around 250 billion m³ which is about 38.55% of 1123 billion m³ usable water (Bhat, 2014); while in Saudi Arabia, groundwater constitutes 80% of the total usable water (2259 billion m³) (Aly et al. 2013).

In comparision to surface water, groundwater is a main source of water supply for many communities' in different countries and regions, because of its some advantages like stable spatiotemporal distribution, low or no bacteriological contamination, better water quality, low turbidity, constant water temperature and closeness to the community (Tai et al. 2012). However, it is mostly polluted because of human activities (industrial effluent, wastewater irrigation, land cover change and urbanization), and agriculture activity (excessive use of fertilizer and pesticide) (Qian et al. 2014; Qian et al. 2016; Nigus et al. 2020; Bhalme and Nagarnaik, 2012). There are also natural factors like geologic structures and hydrogeological settings that may also cause variations in hydro-chemical characteristics of groundwater (Nigus et al. 2020; Yahong et al. 2016).

Ions in excess amounts are causes for groundwater pollution. These are nitrogen pollution (Kuhr et al. 2013; Jalali, 2011), fluorine pollution (Daniele et al. 2013; Feifei et al. 2021; Wu and Sun, 2015), arsenic pollution (Nasrabadi and Bidabadi, 2013), organic contamination (Han et al. 2013), hardness pollution (salts of Ca and Mg) (Muhammad et al. 2013; Yahong et al. 2016), and sodium and sulfate pollution (Yahong et al. 2016). Studies also reported contamination of groundwater with pathogens such as escherichia coli, enterobacter, streptococcus, salmonella and shigella spp (Nchofua et al. 2020). Studies conducted in the rural areas of Ethiopia indicated that wells have high level of microbal contamination (E. coli) (Mengesha et al. 2004; Tsega et al. 2014).

Based on a study conducted in Thailand in Ubon Ratchathani province, groundwater samples were identified with higher concentration of lead (maximum of 66.9µg/L) and zinc (maximum of

 $302\mu g/L$) (Wongsasuluk et al. 2014). A study conducted in China revealed a higher concentration of Mg²⁺ (54.72 mg/L), SO₄²⁻ (355.42 mg/L) and NO³⁻ (43.60 mg/L) in groundwater samples (Nigus et al. 2020). There were also other studies that groundwaters showed higher concentration of arsenic (maximum of 420µg/L) (Nasrabadi and Bidabadi, 2013), fluoride (4.3 mg/L) (Daniele et al. 2013), and total hardness (785.34 mg/L) (Nigus et al. 2020).

A study conducted in China showed that Water Quality Index (WQI) values for groundwater samples varied between 58.37 and 246.23, with an average value of 103.07. Among 31 samples, 67.74% of groundwater samples were of medium quality and identified as suitable for drinking purposes. The water quality of six groundwater samples (19.35%) and four groundwater samples (12.9%) were poor and extremely poor, respectively, and considered unfit for drinking (Daniele et al. 2013; Feifei et al. 2021; Wu and Sun, 2015). Another study conducted on shallow groundwater identified that out of the 34 sample sites, 10 groundwater sample sites (29.4%) had good quality, 19 sample sites (55.9%) were classified as fair quality, 5 sample sites (2.9% and 11.8%) were identified to have poor and very poor quality, respectively (Nigus et al. 2020).

Groundwater is used for drinking in the Rift Valley part of Ethiopian (Ramya, 2018). Researchers studied the groundwater chemistry in the Ethiopian Rift Valley and ravealed that their chemical compositions were different (Ayenew, 2008; Ayenew et al. 2008; Shankar and Nafyad, 2019; Yitbarek et al. 2012). Volcanic aquifers were identified as sources of fluoride in the great Rift Valley groundwater (Furi et al. 2011). In addition, liquid waste discharges from cities were identified as groundwater pollutants in the Rift Valley (pollution of groundwater in the Dire Dawa groundwater basin) (Taye, 1988). Tamiru, 2004 reported that untreated waste discharge to rivers were causes for pollution of groundwater in Addis Ababa (Tamiru, 2004). Dinka et al. (2015) found that anthropogenic activities caused pollution of groundwater in Matahara region.

A rapid assessment of drinking water quality in Ethiopia reported a high nitrate and fluoride concentration in more than 30% of water sources (Dagnew et al. 2007). Treatment of contaminated groundwater requirses adequate knowledge and skill, and it is costly (Hasan, 2014). Regular monitoring and detailed studies of groundwater quality provides an early warning before further contamination and hence expensive cleanup is need. There is not much study conducted around the study area on groundwater quality, but majority of the communities rely on groundwater for

drinking purpose. Hence, variations in groundwater quality were investigated on 7 handpumps selected in the study area. This may serve indicators of groundwater quality of the town and the nearby towns.

2. METHODS AND MATERIALS

2.1. Study area

This study was conducted on seven hand pumps in Holte town, Derashe Special Woreda. However, the lab analysis was done at Arba Minch University in southern Ethiopia on June 7-8, 2022 (Fig. 1). Holte town was established on March 3, 2010 GC. It is bordered with Gato town in the South, Wozeka town in the North, Gomayide town in the East and Gidole town in the West. It is situated at about 547 Km South West of Addis Ababa, 326 Km away from Hawassa city, and 50 km southwest of Arba Minch. The town covers an area of 7.1 km². It is situated on plain landforms within the great Ethiopia Rift Valley and stretches from 1110m up to 1190m above sea level. The town experiences a mean annual temperature with the range of 15^oc to 27^oc, grouped in the "Kola" climate (weather condition) of the country (Tilahun et al. 2022). In 2013, the town has a total population of 20,416 of which 10,953 were females and 9,463 were males. There are about 2,783 households in the town. The town has 7 villages. The people of the town mainly use groundwater wells installed as hand pumps for different domestic purpose.



Figure 1: Map of Ethiopia, SNNPR, Derashe special woreda and Holte town, respectively.

2.2. Sample collection and analysis

Groundwater samples were collected from purposively selected 7 hand pumps at different seven sites in the town. The seven hand pumps were selected purposively because of their coverage throughout the town. The samples were collected using a sterilized 1 L sample bottles based on the sampling procedure of the American Public Health Association (APHA, 2005). Each of groundwater sample were analyzed in Arba Minch University Water Quality Lab for various physicochemical parameters, such as pH, EC (electrical conductivity), total dissolved solids (TDS), calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), potassium (K⁺), chloride (Cl⁻), sulfates (SO4²⁻), fluoride, bicarbonate (HCO₃⁻), total alkalinity and total hardness. The standard procedures recommended by WHO were used (WHO, 2011). The details were described in Table 2.

No.	Parameters to be measured	Measuring method
1	рН	pH meter
2	Total dissolved solids (TDS)	Gravimetric method
3	Electrical Conductivity (EC)	Conductivity meter
4	Potassium (K ⁺)	Flame Photometric Method
5	Sodium (Na ⁺)	Flame Photometric Method
6	Calcium (Ca ²⁺)	Titration method
7	Magnesium (Mg ²⁺)	Titration method
8	Chloride (Cl ⁻)	Titration method
9	Bicarbonate (HCO ₃ ⁻)	Titration method
10	Sulfate $(SO_4^{2^-})$	Spectrophotometric Method
11	Fluoride (F ⁻)	Spectrophotometric Method
12	Total Hardness (TH)	Titration method
13	Total alkalinity (TA)	Titration method

Table 1. Method employed to measure parameters in ground water

2.3. Quality control

To assure the data quality, the result of physicochemical analysis was checked with the anioncation balance. The principle of the anion cation balance is that the sum of cations and sum of anions are equal because the solution must be electrically neutral. In an electrically neutral solution, the sum of the cations should be equal to the sum of anions in milli-equivalent per liter (Gebrerufael et al. 2019; Hounslow, 1995). Based on the electro neutrality, analysis of water samples with a percent balance error $< \pm 5\%$ is regarded as acceptable (Fetter, 2001; Gebrerufael et al. 2019). The cations and anions balance results of the water samples analysis from Holte town are reliable as the charge balance error for more than 95% of the groundwater samples fall within the accepted limits of $< \pm 5\%$. Laboratory analysis result of the 7 groundwater samples were used to determine the groundwater chemistry of Holte town.

The analysis per each parameter of a sample was conducted in triplicate (Jagaba et al. 2020) and the average was taken to assure the quality of the data and to check the accuracy of the experimental results.

2.4. Hydro-chemical facies and evolution mechanisms

Water chemistry is influenced by water-rock interaction taking place from the recharge area to sampling location (Purushothaman et al. 2014). Hydro-geochemical types reflect the effects of

chemical reactions occurring between the minerals within the lithological framework and groundwater (Varol, 2015). In this study, the groundwater samples were classified hydrochemically using major cations and anions with conventional Piper tri-linear diagram to determine the similarities between groundwater in the area. In addition, the Gibbs diagram was used to understand the genesis of groundwater. The present study used Piper tri-linear and Gibbs diagram similar to other studies (Şehnaz, 2017).

2.5. Calculation of water quality index (WQI)

In this study, WHO standards of 2011 adopted from previous studies were used to compute the WQI's for different physicochemical parameters by the Weighted Arithmetic Index method (Jagaba et al. 2020; Tiwari, 1985) to assess the suitability of groundwater in the study area for drinking purposes. It requires three important parameters like assigned weight to each parameters, relative weight of each parameter in relation to others and quality rating scale (Brhane, 2018). Different researchers have reported variable weights assigned to a particular water quality parameter. Based on the literature, this study assigned weight values ranging from 1 to 5 (Tables 6), where 5 meant most significant and 1 less significant. The relative weights, quality rating scale and water quality index (WQI) were determined using the following equations (Jagaba et al. 2020; Vasanthavigar et al. 2010; Feifei et al. 2021; Gebrerufael et al. 2019; Tirkey et al. 2017).

$$W_i = \frac{W_i}{\sum W_i}, i \text{ start from 1 up to n.....(1)}$$

Where

- W_i is the relative weight
- \blacktriangleright w_i is the weight of each parameter
- ▶ *n* is the number of parameters.

Tables 6 and 7, also highlights the relative weight for each parameter as computed. For each of the parameters, a quality rating scale (qi) was determined using the relationship in Equation (2) below:

Where

- 4 q_i is the quality rating
- $\mathbf{4}$ C_i is the concentration of each chemical parameter in (mg/L)
- $\mathbf{4}$ S_i is the WHO drinking water standard for each of the parameters

The sub-index and WQI were computed using the relationship in Equations (3) and (4) respectively

 $SI_i = w_i \times q_i$(3).

Where,

- SI_i is the sub-index of the i^{th} parameter
- q_i is the rating based on the concentration of the i^{th} parameter

After calculating the WQI, the following ranges were used to categorize the water quality type as excellent, good, poor, very poor and unsuitable for drinking (table 3).

Table 2. Water Quality Index use and the status of respective groundwater (Şehnaz, 2017)

Range	Water Type
<50	Excellent water
50-100	Good water
100–200	Poor water
200-300	Very poor water
>300	Water unsuitable for drinking purposes

2.6. Data analysis

Data were analyzed by using statistical package for social science (SPSS.version.23), and Excel 2010. Statistical measures (descriptive statistics) of the groundwater quality parameters were determined by using the SPSS software ver. 23. Cations and anions were also calculated (Table 5). Microsoft Excel was employed for plotting graphs (Piper diagram and Gibbs diagram). The data were displayed using the parameters of the minimum value, maximum value, and mean value. The results/findings of the study were finally displayed using tables and graphs

3. RESULTS AND DISCUSSION

3.1. Descriptive statistical results

Lab result and descriptive statistics of 13 physicochemical parameters of groundwater in the study area were summarized (Table 4 and 5). The analysis result indicated that the pH ranged from 7.8–8.1, which was slightly basic/alkaline. The TDS and EC of the groundwater samples varied from 1790 to 2500 mg/L and 3580 to 4980µs/cm, respectively.

Mean/average of each cation for all samples occured in the order of $Ca^{2+} < Mg^{2+} < K^+ < Na^+$ and mean/average of each anion concentrations were in the order of $F^- < SO_4^{2-} < Cl^- < HCO_3^-$. Krishna, (2019) that reported anion concentration as $F^- < SO_4^{2-} < Cl^- < HCO_3^-$. This was in conformity with the finding of the current study. However, Igibah (2019) reported that groundwater quality showed wide spatial variations owing to human and agricultural effects with an anion order of $SO_4^{2-} > HCO_3^- > F^- > Cl^-$. This was contrary to the finding of current study. In table 4, SL from 1 to 7 indicates the 7 sample locations

No	Parameter	Unit	The seven ground water sample						
			SL1	SL2	SL3	SL4	SL5	SL6	SL7
1	Total Alkalinity	mg/L	776	780	800	680	600	804	920
2	Bicarbonate alkalinity (HCO ₃ ⁻)	mg/L	776	780	800	680	600	804	920
3	Chloride (Cl ⁻)	mg/L	150.0 2	90.80	465.86	51.32	61.19	73.04	84.88
4	Total hardness	mg/L	180	168	412	172	228	132	112
5	Electrical conductivity (EC)	µs/cm	4220	4030	4980	3700	4450	3800	3580
6	Total dissolved solids (TDS)	mg/L	2112	2019	2500	1800	2234	1900	1790
7	Calcium (Ca ²⁺)	mg/L	16.03	20.84	28.86	28.86	22.44	8.02	4.81
8	Magnesium (Mg ²⁺)	mg/L	34.02	28.19	82.62	24.3	41.8	27.22	24.3
9	Fluoride (F ⁻)	mg/L	0.17	0.03	0.01	0.01	0.01	0.00	0.21
10	Sulfate (SO ₄ ²⁻)	mg/L	21.47	18.82	17.65	17.65	7.06	17.94	15.88
11	рН	pH scale	8.00	8.00	7.80	8.00	7.90	8.10	8.10
12	Sodium (Na ⁺)	mg/L	331.8	289.2	461.2	264.4	184.8	334.8	335.8
13	Potassium (K ⁺)	mg/L	47.2	53.6	134	56.4	10.5	55	53.2

Table 3. Quality of seven groundwater samples analyzed at Arba Minch University, Water Quality Laboratory, southern Ethiopia in June, 2022. All units is mg/L, except pH and conductivity (μ s/cm).

Parameters	Range	Mean	WHO limit (WH O, 2011)	Ethiopia n limit (ES Agency, 2013)
pН	7.8-8.1	7.99	6.5-8.5	6.5-8.5
Total dissolved solids (TDS)	1790–2500	2051	1000	1000
Electrical conductivity (EC)	3580-4980	4109	1500	
Total Hardness (TH)	112–412	201	300	300
Total Alkalinity (TA)	600–920	766	500	200
Calcium (Ca ²⁺)	4.81-28.86	18.55	300	75
Magnesium (Mg ²⁺)	24.3-82.62	37.49	50	50
Sodium (Na ⁺)	184.8-335.8	314.57	200	200
Potassium (K ⁺)	10.5–134	58.56	12	1.5
Fluoride (F ⁻)	0.00-0.21	.06	1.5	1.5
Sulfate (SO ₄ ²⁻)	7.06-21.47	16.64	250	250
Chloride (Cl^-)	51.3-465.9	139.59	250	250
Bicarbonate (HCO_2^{-})	600–920	766	500	

Table 4. Comparison of lab results with WHO and Ethiopian standards of drinking water quaity, Arba Minch City, southern Ethiopia in June, 2022. All units is mg/L, except pH and conductivity (μ s/cm).

Chemical characteristics of ground water

3.2. Chemical characteristics of ground water

3.2.1. Major Cations in the groundwater of the town

a. Calcium (Ca²⁺) concentration

Calcium (Ca²⁺) in the water samples determined groundwater hardness. It also functioned as a pH stabilizer and also gave water a better taste. According to WHO and Ethiopian standards, the maximum permissible limit for Ca²⁺ in drinking water must be 300 mg/L and 75 mg/L, respectively. The result of this study showed that all groundwater samples analyzed were found within the permissible limit of drinking water between 4.81–28.86 mg/L (Table 5). Its spatial distribution in the study area was shown in Fig. 2A.

b. Magnesium (Mg²⁺) concentration

According to WHO and Ethiopian standards, the maximum permissible limit for Mg^{2^+} in drinking water should be 50 mg/L (Table 5). The value of Mg^{2^+} in groundwater was found above 50 mg/L in *sample location (SL) 3* (82.62 mg/L). Concerning Mg^{2^+} content of the groundwater's, almost all the groundwater samples were found to be suitable for drinking except the one found in *sample location (SL) 3*. Basalt that contained ferromagnesian minerals such as olivine, pyroxenes, and amphibole were identified as a source of Mg^{2^+} (Shankar and Nafyad, 2019; Wagh et al. 2019). The higher concentration of Mg^{2^+} in *location (SL) 3* might be due to the presence of the basalt that contained ferromagnesian minerals. Its spatial distribution in the study area was shown in Fig. 2B.

c. Sodium (Na⁺) concentration

According to WHO and Ethiopian standards, the maximum permissible limit for Na^+ in drinking water ought to be 200 mg/L. Sodium concentration was higher in all sampled sites beyond the limit except *sample location (SL) 5* (184.8 mg/L). Deep percolation of water from the topsoil layers might be the possible source of sodium owing to its longer residence time and water-rock interactions (Shankar and Nafyad, 2019; Wagh et al. 2019). Its spatial distribution in the study area was shown in Fig. 2D.

d. Potassium (K⁺) concentration

According to WHO standard of 2011 and Ethiopia drinking water quality standard, potassium concentration in drinking water should be below 12 mg/L and 1.5 mg/L to be in a good zone, respectively. Good zone are much more suitable for drinking purposes. The potassium in groundwater of the study area was greater than the standard/beyond the good zone in all sampled areas according to Ethiopia standards except *sample location (SL) 5* (10.5mg/L) based on WHO limit. Since the areas were previousely farmlands, the source of potassium might be the leaching of potassium fertilizer through the soil or due to the dissolution of potassium rich minerals. The spatial distribution in the study area was shown in Fig. 2C.



Figure 2. Spatial distribution maps of (a) Calcium (b) Magnesium (c) Potassium (d) Sodium

3.2.2. Major Anions in the groundwater of the town

a. Bicarbonate (HCO₃⁻) concentration

According to WHO standard of 2011, the maximum permissible limit for HCO_3^- in drinking water should be 500 mg/L. In the study area, bicarbonate concentration was very high in all sampled areas of the town. Studies indicated that silicate and carbonate weathering processes were sources of bicarbonate (Bala, 2005). All part of the study area had HCO_3^- concentration more than 500 mg/L. The possible source of HCO_3^- could be the magmatic release of CO_2 by the active fault zones (Shankar and Nafyad, 2019; Mechal et al. 2017). The spatial distribution in the study area was shown in Fig. 5A.

b. Chloride (Cl⁻) concentration

According to WHO standards of 2011 and Ethiopian water quality standards, the maximum permissible limit for Cl⁻ in drinking water ought to be 250 mg/L. All of the chloride concentration in groundwater in the study area was below the recommended WHO standard except *sample location (SL) 3* (465.86 mg/L). Chloride originates from water-soluble chloride salts present in minerals. Rainwater, weathering and leaching of domestic effluents are sources of chloride in water. At higher concentration chloride damages metallic pipes and gives water a salty taste. The spatial distribution in the study area was shown in Fig. 3.



Figure 3. Spatial distribution map of chloride

c. Sulphate (SO₄²⁻) concentration

According to WHO standards of 2011 and Ethiopian water quality standards, the maximum permissible limit for SO_4^{2-} in drinking water should be 250 mg/L. In the study area, all of the samples had the prescribed limit for drinking purposes. The spatial distribution in the study area was shown in Fig. 4A.

d. Fluoride (F⁻) concentration

According to WHO standards of 2011 and Ethiopian water quality standards, the maximum permissible limit for F^- in drinking water ought to be 1.5 mg/L. Fluoride concentration in groundwater was within the desirable limit of WHO standards and Ethiopian standard in the study area. The result of this study was supported by findings of other study conducted on groundwater in Ethiopia (Shankar and Nafyad, 2019). The spatial distribution in the study area was shown in Fig. 4B.



Figure 4. Spatial distribution maps of (a) Sulfate (b) Fluoride (c) pH (d) Total dissolved solid



Figure 5. Spatial distribution maps of (a) bicarbonate (b) total hardness (c) total alkalinity (d) electrical conductivity

3.3. Other Chemical Constituents in the Groundwater of the Study Area

A. Total Dissolved Solids Concentration

The suitability of groundwater for drinking should be determined based on the concentration of TDS value of less than 1000 mg/L according to WHO standards of 2011 and Ethiopian water quality standards. The TDS value in all the groundwater samples were higher than the standards. These values indicated that there was a high content of soluble salt in the groundwater samples which can't be used for drinking may be due to its unknown health risk. The spatial distribution in the study area was shown in Fig. 4D.

B. pH of the groundwater in the study area

According to WHO standards of 2011 and Ethiopian water quality standards, the standard pH value in drinking water ought to be between 6.5 and 8.5. All the pH value in groundwater of the study area was below the recommended standard. The spatial distribution in the study area was shown in Fig. 4C.

C. Electrical conductivity (EC) of groundwater samples in the study area

Electrical conductivity is used to measure an ability to conduct electric current through dissolved salts that is found in groundwater which helps to know the enrichment of dissolved salt content in the groundwater. The presence of an excess amount of charged particles would limit the quality of groundwater desirability for drinking purpose. According to WHO standards of 2011, the maximum permissible limit for EC in drinking water should be 1500 mg/L. The value of EC in groundwater in the study area was above the standard in all groundwater samples. The spatial distribution in the study area was shown in Fig. 5D.

D. Total hardness (TH) of groundwater samples in the study area

Water hardness (TH) is caused by the existence of cations in water, specifically calcium and magnesium, and anions like carbonate, bicarbonate, chloride, and sulfate. It is known by precipitation of soap scum and requires additional use of soap to accomplish cleaning purpose. According to WHO standards of 2011, the maximum permissible limit for TH in drinking water should be 300 mg/L. The value of TH in groundwater in the study area was below the standard in all groundwater samples except *sample location (SL) 3* (412 mg/L). The spatial distribution in the study area was shown in Fig. 5B.

E. Total Alkalinity(TA) of groundwater samples in the study area

Alkalinity is important water quality parameters used to measure the capacity of neutralized acids. According to WHO standards of 2011, the maximum permissible limit for TA in drinking water ought to be 500 mg/L and 200 mg/L, respectively. The value of TH in the groundwater of the study area was above the standard in all groundwater samples. The spatial distribution in the study area was shown in Fig. 5C.

3.4. Hydro-geochemical facies

The chemical composition of the analyzed groundwater samples of the study area was represented by plotting them in the Piper tri-linear diagram. These diagrams reveal the distribution of the groundwater samples in different subdivisions of the diamond-shaped field of the piper diagram, the analogies, and dissimilarities. The dominant groundwater type of the study area was the mixed Ca–Na–HCO₃ type and Na–HCO₃ type (Fig. 6). Studies reported that Na/Ca–HCO₃ water is dominant in escarpment and Na–HCO₃ type of water is dominant in the rift floor (Kawo and Shankar, 2018; Shankar and Nafyad, 2019). Hot springs and groundwater in the rift valley has a Na–HCO₃ water type, with high Na⁺ and HCO₃^{2–} concentration (Ayenew, 2005; Shankar and Nafyad, 2019). Haji et al. (2018) reported that high concentration of fluoride is related to Na– HCO3 type of waters. However, this was not confirmed in the current study since all the fluoride concentration of the groundwater were within the recommended standards (Table 5).



Figure 6. Hill piper plot (piper diagram) showing the distribution of the groundwater samples in different subdivisions of the diamond-shaped field

3.5. Groundwater evolution mechanisms

Previously, Gibbs diagrams are mainly helpful for the rapid identification of the evolution mechanism of surface waters (Gibbs, 1970), but now, they are widely applied in groundwater studies (Amiri, 2020; Feifei et al. 2021; Somvir, 2017). The diagram for this study was developed using prepared Excel. There are natural factors that control the chemical characteristics of groundwater such as rainfall, evaporation, and water and rock interactions. To understand the groundwater chemistry and the relationship of chemical components of groundwater from their respective aquifers such as chemistry of the rock types, chemistry of precipitated water and rate of evaporation a diagram in which ratios of dominant anions and cations are plotted against the values of total dissolved solids (TDS) was suggested. The result on the diagram is representing the ratio-I for cations $[(Na^+)/(Na^+ + Ca^{2^+})]$ and ratio-II for anions $[Cl^-/ (Cl^- + HCO_3^-)]$ as a function of TDS. This is used to assess the functional sources of dissolved chemical constituents, such as precipitation-dominance, rock-dominance and evaporation dominance (Somvir, 2017).

The data of groundwater samples in this study were plotted on the Gibbs diagram (Fig. 7). The Na⁺/(Na⁺ + Ca²⁺) of all groundwater samples was greater than or close to 0.8, and the Cl⁻/(Cl⁻ + HCO₃⁻) of all samples was less than 0.5. The TDS values of all groundwater samples varied between 1000 and 10000 mg/L. The result indicated that about 50% of samples indicate chemical weathering of rock-forming minerals which influenced the groundwater by means of dissolution of rocks through which water was circulating. But, 50% of samples represented evaporation dominance. Evaporation increases salinity through high concentration of Na⁺ and Cl⁻ might be owing to anthropogenic activities like using fertilizers and irrigation.

Han et al. (2010) using Gibbs diagram indicated that water–rock interactions and rock weathering were the main factors controlling the chemical characteristics of groundwater in some area of Xinzhou Basin. In addition, Somvir, (2017) identified that chemical weathering of rock-forming minerals influenced groundwater quality by means of dissolution of rocks, and evaporation dominance.



Figure 7. Gibbs diagrams of groundwater samples. $(Na^+/(Na^++Ca^{2+}) \text{ and } Cl^-/(Cl^- + HCO_3^-))$

3.6. Water quality index (WQI) result for the groundwater sites

First, 12 important water quality parameters were selected as displayed in Table 6 and a weight was assigned to each parameter depending upon the effect on human health. In addition, the limit values of the World Health Organization's guidelines (WHO) 2011 were utilized in the calculations (Table 6). The highest weight of 5 was assigned to parameters such as Ca⁺² and F⁻ which had the major effects on water quality especially during drinking. $SO_4^{2^-}$, TH and TDS were assigned a weight of 4. EC, pH, Mg⁺², *Cl*⁻ and HCO3- were assigned a weight of 3. Na⁺ and K⁺ were assigned a weight of 2 taking their importance into consideration in water quality. The relative weights (W_i) were computed for each parameter and results were given in Table 6. The WQI values were calculated using related equations (Equations (2)–(4)) (displayed in the methodology section), and WQI results and water types for individual samples were presented in Table 3.

The WHO standards of 2011 was used for the WQI calculation, and weight was given to each parameter and relative weight was calculated. WQI of the study area ranged from 84.4 to 174.3. The result of WQI indicated that about 57.1% (4 out of 7) and 42.9% (3 out of 7) of groundwater samples fell in the category of good and poor water quality, respectively (Table 7). The spatial

distribution of WQI indicated that slightly more than half of the town had good quality of groundwater with some sites having poor groundwater quality.

Parameters	WHO limit	Weight (<i>w_i</i>)	Relative weight
EC	1500	3	0.073
pH	6.5-8.5	3	0.073
TDS	1000	4	0.097
TH	300	4	0.097
Ca ⁺²	300	5	0.122
Mg^{+2}	50	3	0.073
Na ⁺	200	2	0.049
\mathbf{K}^+	12	2	0.049
F⁻	1.5	5	0.122
SO4 ²⁻	250	4	0.097
Cl^{-1}	250	3	0.073
HCO3-	500	3	0.073
		$\Sigma w_i = 41$	$\Sigma W_i = 1.000$

Table 5: Relative weight of chemical parameters

 Table 7: The Calculated WQI value for individual water samples

Sample No.	Sample Site	WQI	Classification
1	Sample Location (SL) 1	104.6	Poor water
2	Sample Location (SL) 2	100.6	Poor water
3	Sample Location (SL) 3	174.3	Poor water
4	Sample Location (SL) 4	94.7	Good water
5	Sample Location (SL) 5	84.4	Good water
6	Sample Location (SL) 6	97.9	Good water
7	Sample Location (SL) 7	97.5	Good water

4. CONCLUSIONS AND RECOMMENDATIONS

The pH values of groundwater were slightly basic in nature (average = 7.99). The pH of groundwater samples indicated alkaline in nature. The EC, HCO_3^- and TDS values of all the samples exceeded the upper limit of WHO standards for drinking water. The chloride concentration in groundwater for all samples of the study area were within the desirable limit of WHO standards except *sample location (SL) 3* which exceeded the maximum allowable limit of 250 mg/L.

The order of abundance of cations in the groundwater was $Ca^{2+} < Mg^{2+} < K^+ < Na^+$ and the order of anionic abundance was $F^- < SO_4^{2-} < Cl^- < HCO_3^-$. Based on the hydro-geochemical facies identified, the majority of the samples were represented by Ca–Na–HCO3 type and Na–HCO3 type of water. The Piper Tri-linear diagram indicated that most of the groundwater samples fell in Mixed Ca–Na–HCO₃ types. Quality of groundwater in the samples was mainly dominated by evaporation while remaining samples were dominated by chemical weathering of rock forming minerals.

The result of WQI indicated that 57.1% (4 out of 7) and 42.9% (3 out of 7) of groundwater samples fell in the category of good and poor groundwater quality, respectively.

Overall, groundwater quality parameters should be monitored and regularly inspected in the riskey areas of sample location (*SL*) *1*, *2 and 3* in Holte town to avoid human health related problems and ensure sustainable socio-economic development. The local government should ensure that land use plans and regulations should protect the local environment and groundwater sources. The residents should be educated about groundwater and the town facilities should have good pollution prevention practices to avoid further environmental degradations. Also, further geochemical and groundwater quality investigations should be carried out to reduce the possibility of groundwater contamination and thus keep the community safer.

Abbreviations

EC: Electrical Conductivity; GW: Groundwater; TA: Total Alkalinity; TH: Total Hardness; TDS: Total Dissolved Solids; WQI: Water Quality Index; WHO: World Health Organization; SL: Sample Location

Authors' contributions

Mr. Demamu Tagele and Dr. Tamru Tesseme carried out the water quality analysis and statistical portion of the study, data analysis, interpretation of results and manuscript writing, reviewed and finalized the manuscript. The authors read and approved the final manuscript.

Funding

No fund was allocated for this study.

Availability of data and materials

All available data are found in the research article.

DECLARATIONS

Ethics approval and consent to participate

The ethical approval was obtained from Arba Minch University, Water Technology Institute, Department of Water Supply and Environmental Engineering.

Competing interests

The authors declare that they have no competing interests.

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