

# Hydrogeochemical and isotopic studies of groundwater in the middle voltaian aquifers of the Gushegu district of the Northern region

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**Abstract** This work is to establish the hydrochemistry and origin of groundwater in some parts of the Gushegu district of the Northern Region of Ghana. Hydrochemical data from 19 groundwater and 7 rock samples have been used to evaluate water quality, water types, and sources of various ions as well as origin of the groundwater. The study results show that the quality of groundwater from the area is generally not good due to their fluoride ( $F^-$ ), bicarbonate ( $HCO_3^-$ ) and electrical conductivity (EC) concentrations. The  $F^-$  contents of the groundwater have values as high as 1.97 mg/L, with 53 % of the groundwater having concentrations of  $F^-$  exceeding the WHO recommended allowable limits. These high  $F^-$  values have the potential of causing serious health problems such as kidney failure, dental and skeletal fluorosis, reproductive problem and reduction in intelligent quotient of consumers. A plot of Gibbs diagram reveals that rock weathering and precipitation are the major hydrogeochemical processes regulating the water chemistry of the study area. Petrographic thin-section analyses of rock samples identify minerals present to be muscovite, plagioclase feldspars, quartz, sericite and iron oxide. Stable isotope ( $^{18}O$  and  $^2H$ ) composition of the waters reveals that most of the groundwater is likely to be recharged from local precipitation, indicating their

meteoric origin. Some samples, however, showed considerable evaporation.

**Keywords** Gushegu · Fluoride · Voltaian aquifers · Muscovite · Sericite · Stable isotopes

## Introduction

The Northern region of Ghana consists of 18 administrative districts with Tamale as its regional capital. Access to enough pipe-borne water in the other districts in the region including the Gushegu district except Tamale is very limited. The Northern region is amongst the poorest and economically deprived regions of Ghana. The Gushegu district is predominantly rural and this has resulted in more than its 300 communities to dwell mainly on rivers, streams, jets, rain waters, dams, hand-dug wells and boreholes. However, increased contamination and pollution of surface waters through natural and anthropogenic activities have prompted the residents to shift their attention mainly to the use of groundwater for their domestic activities. Although groundwater is generally buffered from most surface polluting activities (Yidana and Yidana 2010), its quality can deteriorate with time as a result of increasing pollution of surface waters. (Appelo and Postma 1993) defined water quality as its suitability for human consumption, domestic use and irrigation. The groundwater system in any area varies in chemistry mainly due to chemical alteration of meteoric water recharging the aquifer system (Back 1966; Drever 1988; Hem 1991). According to Gibbs (1970), the possible factors that control water chemistry are weathering of rocks, atmospheric precipitation, evaporation and crystallization. The chemical quality of groundwater depends on the characteristics of

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the soil and rock media through which it passes en route the groundwater zone of saturation (Raji and Alagbe 1997; Acheampong and Hess 1998; Olayinka 1999; Foster et al. 2000). UNESCAP (2000) revealed that 15 out of every 1000 children born in the developing world die before the age of five from diarrhea caused by drinking polluted water. For example, (Apambire et al. 1997) revealed the presence of fluoride as high as 4.6 mg/L in groundwater in the Bongo granites of the Upper East Region of Ghana. This has resulted in the prevalence of dental fluorosis and quiet recently the emergence of skeletal fluorosis in the area. Other negative effects of high fluoride in groundwater include reduction of intelligent quotient and kidney damage.

The Gushegu district is underlain by rocks of the Voltaian Supergroup (Bertrand-Sarfati et al. 1990). The Voltaian Basin is the least in terms of groundwater potential as far as groundwater potential of Ghana is concerned (Dapaah-Siakwan and Gyau-Boakye 2000). Various studies have been carried out in Ghana concerning the characterization of the hydrochemistry of the Voltaian aquifers (Yidana and Yidana 2010). Works by Acheampong and Hess (1998), Yidana et al. (2008) suggest groundwaters of the Southern Voltaian and Afram plains are controlled by weathering of albitic feldspars and silicate minerals, respectively. For example, Yidana et al. (2008) used the mass balance and multivariate techniques to define silicate mineral weathering as the primary control on the hydrochemistry of groundwater from the Afram Plains area. However, these works have been limited to the Southern part of the Voltaian. The Voltaian system is one of the two major hydrogeological formations in Ghana and underlies about 45 % of the total landmass of the country. It is a Paleozoic sedimentary basin comprising sandstones, shale, limestone, conglomerate, mudstone, siltstone and arkoses. The Voltaian system is divided into three main units: the upper Voltaian (made up of massive sandstones and thin-bedded sandstone); the middle Voltaian (comprising of the Obosum and Oti beds); and the lower Voltaian (Junner and Hirst 1946). Minor et al. (1995) and Dapaah-Siakwan and Gyau-Boakye (2000) worked within the Voltaian but focused largely on the general hydrogeology of the area. However, the application of stable isotopes of oxygen and hydrogen ( $^{18}\text{O}$ ) and ( $^2\text{H}$ ) in groundwater control mechanisms in the study area is lacking in literature, far from what has been carried out in other parts of the country and elsewhere beyond the boundaries of Ghana. Stable isotopes of oxygen and hydrogen are particularly useful as tracers of hydrological processes in aquifers since their signatures or compositions are not affected by rock–water interactions at the usual low groundwater temperatures (Marfia et al. 2004) and provide insight and support into comprehensive water resources assessment and management.

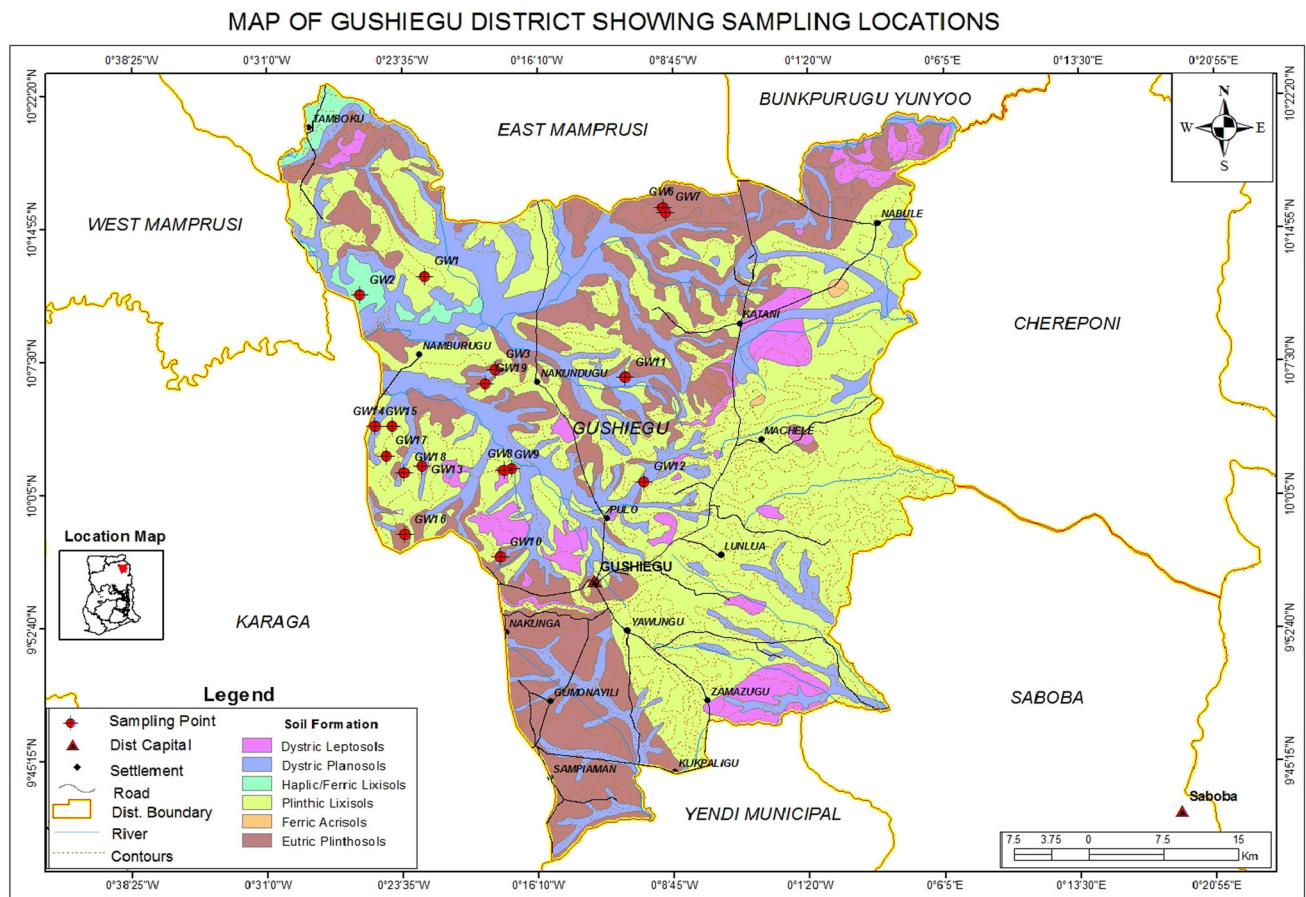
At present, there is no major industry in and around the study area, yet households and municipal wastes are directly discharged into water bodies which may finally end up in the groundwater system. The water supply for human consumption is often directly sourced from groundwater without biochemical treatment and this can cause serious health effects. The Government of Ghana in 2010 launched the Savanna Accelerated Development Authority (SADA) and the construction of the Eastern corridor roads. SADA looks at agricultural development, industrialization, economic and social infrastructure. The study area falls within the jurisdiction of SADA and the Eastern corridor roads also pass through the study area. The construction of roads and implementation of the activities of SADA would open up the area to more business opportunities. The likely emergence of major industries in and around the study area may eventually affect the quality and quantity of water. Hence, there is the need for hydrochemical investigation to determine the quality of the groundwater in the study area, the possible sources of the ions as well as the origin of the groundwater. This will help determine the suitability of groundwater in the study area for drinking water purposes and provide a baseline for future studies of water quality and trends.

### The study area

The Gushegu district lies within longitude  $0^\circ$  and  $45'W$  and latitude  $9^\circ30'$  and  $10^\circ30'N$  and is one of the 18 districts in the Northern region of Ghana. It is much drier due to its proximity to the Sahel and the Sahara. The climate of the study area is tropical and semi-arid. Annual precipitation averages just over 1050 mm, while potential evapotranspiration is about 1770 mm (Pelig-Ba 2000). There are only about 4–6 months of rainfall during the year, from May to October, the rest, from November to May, is relatively dry and hot. After the rainy period, the northeast trade winds, locally termed the harmattan prevails up to February/March. During the period, the weather becomes very dry and hot in the day but cools to less than  $20^\circ\text{C}$  in the night. The study area consists predominantly of the Guinea savannah vegetation, characterized by tall grasses interspersed with drought-resistant trees such as Baobab, Shea, Dawadawa and Acacias (Pelig-Ba 2009). Figure 1 is a map of the study area showing the sampling points.

### Geology and hydrogeology

The study area lies entirely within Pendjari or Oti mega-sequences which represent the middle lithostratigraphic unit, a sub-division of the Paleozoic Voltaian sedimentary formation. It is highly heterogeneous in terms of lithology and dominated by quartzites, shales, mudstones, siltstones,



**Fig. 1** Location map of the study area showing the sampling points

conglomerates, limestones, tillites, barite-bearing dolomitic carbonates and argillaceous and/or calcareous thin-bedded cherts known as silexites. This group overlies the Panabako formation of the Bombouaka mega-sequence or the Lower Voltaian sub-division (Leprun and Trompette 1969; Affaton et al. 1980; Wright et al. 1985; Hoffman 1999). The northern part of the district is underlain by Bombouaka mega-sequence which consists of fine to coarse-grained and more or less feldspathic sandstones (Bertrand-Sarfati et al. 1990).

The rocks that underlie the study area and Ghana in general are essentially impermeable and have little or no primary porosity. Therefore, groundwater occurrence is associated with the development of secondary porosity as a result of jointing, shearing, fracturing and weathering. This has given rise to two main types of aquifers: the weathered zone aquifers and the fractured zone aquifers. (Ministry of Works and Housing 1998).

The hydraulic conductivities ( $K$ ) in the study area range from 0.05 to 3.39  $\text{m day}^{-1}$ , while the transmissivity values also ranges from 0.17 to 23.00  $\text{m}^2 \text{day}^{-1}$ . Porosity values of the rock samples ranges between 3.9 and 9.7 %. Screen

lengths for boreholes in the study area ranged from 4.00 to 31.70. According to Dapaah-Siakwan and Gyau-Boakye (2000), the yield of boreholes within the study area ranges between 0.41 and 9  $\text{m}^3/\text{h}$ , with an average yield of 6.2  $\text{m}^3/\text{h}$ .

### Materials and methods

A total of nineteen (19) groundwater samples consisting of seventeen (17) boreholes and two (2) hand-dug wells were sampled at various locations following standard protocols as described by Barcelona et al. (1985). Electrical conductivity (EC) and Total Dissolved Solids (TDS) were determined in the field on all samples using the Hach Sension5. pH and Temperature were also measured in the field using the Hach Sension1. Locations of selected sampling points were determined using the Garmin Vista CP GPS. In sampling from boreholes with hand pumps, purging was done for at least ten (10) min to flush stagnant water retained in the pipes. In the case of hand-dug wells, it was properly checked and confirmed that the well was being used daily. This was to ensure that stale and stagnant

water was not sampled. 330 ml preconditioned polyethylene bottles were used in collecting duplicate water samples. The samples for cations were filtered on site through a 0.45  $\mu\text{m}$  filter of acetate cellulose and immediately acidified to a pH less than 2 by addition of Merck TH Ultra-pure nitric acid. The samples for anions were only filtered but not acidified. All water samples were correctly labeled, kept air-tight to prevent evaporation and kept in a refrigerator (except those for isotopic studies) until analyses were carried out. All water analyses were carried out at the chemistry laboratory of the Ghana Atomic Energy Commission (GAEC), Kwabenya. Thin-section preparation was carried out at the Geological Laboratory of the Earth Science Department, University of Ghana.

Major ions such as Sodium ( $\text{Na}^+$ ) and Potassium ( $\text{K}^+$ ) were analyzed in the laboratory using the flame photometer (Sherwood model 420 with detection limit of 0.001, Eaton et al. 2005). Calcium ( $\text{Ca}^{2+}$ ) and Magnesium ( $\text{Mg}^{2+}$ ) were analyzed using the AA240FS Fast Sequential Atomic Absorption Spectrometer as prescribed by Eaton et al. (2005), Broekaert (1998), Sperling and Welz (1999) and Sood et al. (2004). The ICS-90 Ion Chromatograph (DIONEX ICS-90) was employed in the analysis of Chloride ( $\text{Cl}^-$ ), Fluoride ( $\text{F}^-$ ), Nitrate ( $\text{NO}_3^-$ ), and Sulfate ( $\text{SO}_4^{2-}$ ). The detection limit and accuracy is 0.0001 mg/L and 95–105 %, respectively. Phosphate ( $\text{PO}_4^{3-}$ ) was determined by the ascorbic acid method using the ultraviolet spectrophotometer (UV-1201). The accuracy of the results was confirmed by employing the Charge Balance Error (CBE) as employed by Freeze and Cherry (1979).

## Results and discussions

Table 1 presents a statistical summary of the hydrochemical parameters. Detailed hydrochemical parameters are also presented in Table 2.

Temperature variation in the study area is presented in Table 1. The difference in temperature could be attributed to the variation in sampling time and season of the sampling. The lowest and highest temperatures were recorded early in the morning and afternoon, respectively. All the sampling was carried out in six days within the month of October, 2010 just at the onset of the dry season.

The pH of the water samples analyzed in the study area ranges from weakly acidic to slightly alkaline (pH of 6.93–7.31), with a standard deviation of 0.09. All the samples fall within the WHO (1996) recommended allowable limits of 6.5–8.5 for pH of drinking water.

There is variation in electrical conductivity (EC) of groundwater in the study area ranging from 79.10  $\mu\text{S}/\text{cm}$  at Gindigiri to 1663  $\mu\text{S}/\text{cm}$  at Makendaya, with a mean of 885.44  $\mu\text{S}/\text{cm}$ . Of the 19 samples collected, 31.6 % have

conductivity values within the WHO (1996) maximum allowable limit of 700  $\mu\text{S}/\text{cm}$ , while 68.4 % are above the maximum limit. The very high conductivities recorded for some areas may be as a result of increased farming activities which introduce ions and metals from agrochemicals such as fertilizers from farmlands. Furthermore, the higher conductivities in most of the groundwater could also be as a result of higher temperatures (average of 30.37  $^\circ\text{C}$ ); the warmer the water, the higher the conductivity. On the basis of conductivity, groundwater in the study area is generally not potable.

The total dissolved solids (TDS) in the study area vary from 37.70 to 835 mg/L. The lowest and highest TDS values are recorded at Gindigiri and Makendaya, respectively. Makendaya also happens to be the same location where the highest EC value was recorded. The mean TDS is 440.68 mg/L. The low TDS values recorded in the study area could be as a result of the absence of heavy industries in the Gushegu district that release industrial effluents to contaminate the groundwater and increase the TDS. Therefore, the possible sources for TDS in the district may include agricultural run-off and natural sources such as silt, plankton, and the geology. The WHO (1996) recommended maximum allowable limit for TDS in drinking water is 1000 mg/L,

Davis and Dewiest (1966) and Freeze and Cherry (1979) classified groundwater with TDS values within the range 0–1000 mg/L as fresh, 1000–10,000 mg/L as brackish, 10,000–100,000 mg/L as saline water and more than 100,000 mg/L as brine. Based on this classification, groundwater in the study area is fresh and potable.

Water hardness is a measure of the total concentration of calcium and magnesium ions and to a lesser extent, the salts of other minerals. Hardness in the study area varies from 20 to 232 mg/L, with mean and standard deviation of 105.52 and 62.60 mg/L, respectively. The lowest value of 20 mg/L was recorded at Nasingbung B1, whilst Makendaya recorded the highest value of 232 mg/L. The WHO (1996) recommended allowable limit for hardness is 500 mg/L. The generally low hardness values recorded could result from the low concentrations of calcium and magnesium in the groundwater. Table 3 represents the classification of groundwater samples based on hardness values.

Out of the 19 samples analyzed, 37 % are soft, 21.05 % are moderately hard, 31.5 % are hard and 10.5 % are very hard. Thus, majority of the samples are within the moderately hard to very hard category and as such cannot be classified as potable.

The  $\text{HCO}_3^-$  values range from 18.32 to 793.19 mg/L with a mean of 430.46 mg/L. The lowest bicarbonate value of 18.32 mg/L occurs at Gindigiri, whilst the highest value of 793.19 mg/L occurs at World Vision Guest House.



**Table 1** Statistical summary of hydrochemical parameters

Parameter	Unit	Minimum	Maximum	Mean	STD	WHO (1996)
Temperature	(°C)	25.10	32.80	30.37	2.09	22–29
pH	(pH units)	6.93	7.31	–	0.09	6.0–9.0
TDS	(mg/L)	37.70	835	437.52	252.95	1000
Conductivity	( $\mu$ S/cm)	79.10	1663	885.44	454.85	700
Hardness	(mg/L)	20	232	105.52	62.60	500
Na <sup>+</sup>	(mg/L)	12.94	320.48	148.49	111.30	200
K <sup>+</sup>	(mg/L)	0.46	63.83	10.09	13.94	30
Ca <sup>2+</sup>	(mg/L)	4.36	48.88	20.58	12.66	200
Mg <sup>2+</sup>	(mg/L)	2.47	16.99	9.19	5.11	150
HCO <sub>3</sub> <sup>-</sup>	(mg/L)	18.32	793.19	430.46	256.59	380
SO <sub>4</sub> <sup>2-</sup>	(mg/L)	4.75	73.96	22.87	17.78	200
Cl <sup>-</sup>	(mg/L)	4.68	121.32	21.70	26.10	250
NO <sub>3</sub> <sup>-</sup>	(mg/L)	0.20	3.03	1.36	0.94	10
PO <sub>4</sub> <sup>3-</sup>	(mg/L)	0.00	0.42	0.08	0.12	<0.3
F <sup>-</sup>	(mg/L)	0.00	1.97	0.89	0.83	1.5

Davis and Dewiest (1966) observed that most bicarbonate ions in groundwater are derived from carbon dioxide in the atmosphere, CO<sub>2</sub> in the soil and solution of carbonate rocks. The recommended allowable limit of HCO<sub>3</sub><sup>-</sup> in water by the WHO (1996) is 380 mg/L. The HCO<sub>3</sub><sup>-</sup> concentrations in the study area are generally high, with 53 % exceeding the maximum allowable limit set by the WHO. The source of the HCO<sub>3</sub><sup>-</sup> could be from the solution of carbonate rocks in the study area. On the basis of the WHO (1996) recommended limit for HCO<sub>3</sub><sup>-</sup>, the groundwater is generally not potable.

Sulfate concentration in the study area varies from 4.75 to 73.96 mg/L. The mean concentration is 22.87 mg/L. The lowest value was recorded at Pumo B2 with Mongoli B2 recording the highest value. Sulfate concentrations in natural waters are usually between 2 and 80 mg/L, although they may exceed 1000 mg/L near industrial discharges (Chapman 1992). High concentrations greater than 200 mg/L may make water unpleasant to drink. The WHO (1996) recommended guideline for sulfate in groundwater is 200 mg/L. The waters could be said to be potable with respect to sulfate concentration.

Phosphate concentration in the study area varies from below detection limit (BDL) to 0.42 mg/L. The mean concentration is 0.09 mg/L. The phosphate concentrations are generally low, below the WHO (1996) recommended limit of 0.3 mg/L. This makes the water generally potable (Table 4).

Waring (1949) indicated that most nitrate water comes from organic sources or from industrial and agricultural chemicals. Various researchers have also attributed elevated concentrations of nitrate to nearby septic tanks (Hem 2002). Nitrate concentration in the study area ranges from

0.20 to 3.03 mg/L with a mean of 1.36 mg/L. The nitrate concentration is low; below the WHO (1996) recommended limit of 10 mg/L. Makendaya recorded the lowest nitrate value, whilst the highest value was recorded at Gushegu Secondary School B2. The water from Makendaya is from deep borehole which is relatively well protected from surface polluting activities. The low nitrate values in the groundwater make them generally potable. Although the value is below the permissible limit, it would require constant monitoring to check the nitrate values.

Chloride content in the study area varies from 4.68 to 121.32 mg/L with a mean of 21.70 mg/L. The highest chloride concentration of 121.0 mg/L occurs at Makendaya, which still remains below the WHO (1996) recommended limit of 250 mg/L. On the basis of chloride concentrations, the water could be said to be potable.

Sodium ions (Na<sup>+</sup>) concentrations varies between 12.94 and 320.48 mg/L with a mean of 148.49 mg/L. Gindigiri recorded the lowest Na<sup>+</sup> concentration with Mongoli B1 recording the highest concentration. 57 % of the 19 groundwater samples analyzed fall within the WHO guideline limit of 200 mg/L, whereas 43 % exceeds the WHO guideline limit. Generally, Na<sup>+</sup> concentrations in the groundwater are below the WHO (1996) maximum permissible limits. However, the 43 % value could pose a health hazard.

Potassium (K<sup>+</sup>) concentration in the study area ranges from 0.46 mg/L at Gushegu Agriculture office to 63.83 mg/L at Salaa B2. The mean is 10.09 mg/L. The concentrations of potassium in natural waters are usually less than 10 mg/L (Chapman 1992). The potassium concentration in the study area is generally low except for Salaa B2 which records higher value above the WHO limit of 30 mg/L. This makes the water potable.

**Table 2** Hydrochemical data from the study area

Locality	Sample id	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>2-</sup>	Fgw	pH	TEMP	EC	TDS	CBE
Tinguri	GW1	267.9	4.6	12.08	7.4136	689.09	19.512	25.071	0.508	0.001	1.57	7.31	31.6	1385	706	4.2304
Salaa 1	GW2	31.75	10.488	11.248	6.9424	143.86	15.648	7.3508	0.953	0.16	0	6.93	30.1	316	151.9	-2.321
Salaa 2	GW3	29.76	63.828	24.968	9.6288	243.88	12.38	23.911	0.799	0.42	1.59	7.27	29.4	590	285	0.2261
Mongoli 1	GW4	320.5	12.72	13.552	3.3636	687.96	65.24	18.191	0.868	0.001	0.3	7.04	31.4	1198	691	5.7182
Mongoli 2	GW5	77.65	5.312	18.72	4.7848	221.41	73.96	5.36	0.414	0	1.63	7.04	31.6	1134	567	-4.795
Nasingbung 1	GW6	15.98	11.304	5.416	2.7848	65.19	19.04	4.68	1.402	0.25	0.06	7.04	31.2	187.3	77.3	-4.972
Nasingbung 2	GW7	91.25	9.564	18.304	8.5788	354.52	4.9292	5.1908	0.525	0.04	1.7	7.05	30.9	1166	584	-1.976
Pumo 1	GW8	49.77	5.472	21.36	4.7848	208.55	15.4	11.32	0.454	0.18	1.97	7.04	31.7	925	458	-4.607
Pumo 2	GW9	96.28	3.404	31.8	14.198	380.88	4.7452	11.04	2.038	0.001	1.69	7.07	32.8	745	394	2.3757
Pumo 3	GW10	268.3	3.496	4.36	4.3636	662.3	19.096	18.72	1.995	0.001	1.86	7.08	32.1	911	671	2.0202
Makendaya	GW11	252.2	4.612	48.88	14.9	705.62	19.348	121.32	0.205	0.28	1.53	7.14	32.3	1663	835	-2.081
Gindigiri	GW12	12.94	3.576	6.416	2.4712	18.32	14.98	10.88	2.375	0.001	0.09	7.05	31.4	79.1	37.7	8.5083
Gushegu town 1	GW13	288.4	3.036	21.496	16.992	793.19	25.984	9.2	2.65	0.02	0	7.02	25.3	1527	802	4.2024
Gushegu agric office	GW14	290	0.46	5.832	3.4712	597.54	23.008	27.24	0.456	0.06	1.92	7.07	29.1	942	661	8.8391
Gushegu town 2	GW15	228.6	22.08	26.496	11.629	649.43	23.316	35.76	0.37	0.03	0	7.05	30.7	1078	729	2.5978
Gushegu town 3	GW16	58.47	7.14	32.44	13.414	253	29.048	14.56	2.024	0.001	0	7.03	29.5	982	479	2.2124
Gushegu town 4	GW17	47.73	5.98	12.664	16.1	205.9	7.3488	38.951	2.626	0.05	0.29	7.04	29.6	528	255	-5.693
Gushegu sec. school 1	GW18	214.5	2.852	36.8	13.414	710.29	21.775	12.52	2.188	0.01	0.01	7.06	31.3	1146	767	-0.656
Gushegu sec. school 2	GW19	179.4	11.72	38.104	15.4	613.26	19.688	11.04	3.03	0.001	0.62	7.07	25.1	971	731	1.8695

**Table 3** Classification of groundwater samples based on hardness values

Water hardness (CaCO <sub>3</sub> mg/L)	Water type
0–60	Soft
61–120	Moderately hard
121–180	Hard
>180	Very hard

After Brown et al. (1970)

Calcium is largely responsible for water hardness because it can be found in water as Ca<sup>2+</sup> ions and may negatively influence toxicity of other compounds. Calcium in the study area ranges from 4.36 to 48.88 mg/L, with a mean of 20.58 mg/L. All the samples from the study area have far less Ca<sup>2+</sup> values than the WHO (1996) recommended maximum limit of 200 mg/L. The low Ca<sup>2+</sup> and Mg<sup>2+</sup> values confirm the low hardness recorded and ultimately makes the water potable.

Magnesium concentration in the study area varies from 2.47 to 16.99 mg/L with a mean of 9.19 mg/L. The magnesium concentration in the study area is less than the WHO (1996) recommended limit of 150 mg/L, making the water potable.

The Fluoride concentration in the groundwater varies from below detection limit (BDL) to 1.97 mg/L. The mean and standard deviations are 0.89 and 0.83 mg/L, respectively. The highest fluoride concentration of 1.97 mg/L is recorded at Pumo B1. Out of the 19 water samples analyzed, 52.6 % exceed the WHO (1996) recommended limit of 1.5 mg/L.

### Factors influencing observed trends in the hydrochemistry of the area

Various factors such as the geology of an area, climate and atmospheric depositions control water chemistry. Various works by Ganyaglo et al. (2010), Yidana and Yidana (2010), Kortatsi (2006) and Jalali (2007) have applied the relationship that exists between anions and

cations to identify their possible origin in water. The Gibbs (1970) plot is one of the several plots used to determine the possible factors controlling water chemistry in an area. Figure 2 is a Gibbs diagram which shows most of the major ions plotting in the region of rock dominance, with a few plotting in the precipitation dominance zone. This reveals that rock weathering and rainfall are the major possible hydrogeochemical processes regulating the water chemistry of the study area.

Na<sup>+</sup> correlates positively with Cl<sup>-</sup> albeit weakly (Table 5). This could suggest that other processes other than dissolution of halite contribute mainly to the Na<sup>+</sup> ions in groundwater from the study area. The commonest minerals identified in the rocks in the area include plagioclase feldspars, ranging in composition from Albite (NaAlSi<sub>3</sub>O<sub>8</sub>) to Anorthite (CaAl<sub>2</sub>Si<sub>2</sub>SiO<sub>8</sub>), Quartz, Muscovite and Sericite. The Na ions in the groundwater could be as a result of the weathering of Albite, yielding the metal Na<sup>+</sup> and silica to solution and forms clay minerals such as illite and montmorillonite. Cation exchange could also contribute to the Na<sup>+</sup> ions in the groundwater.

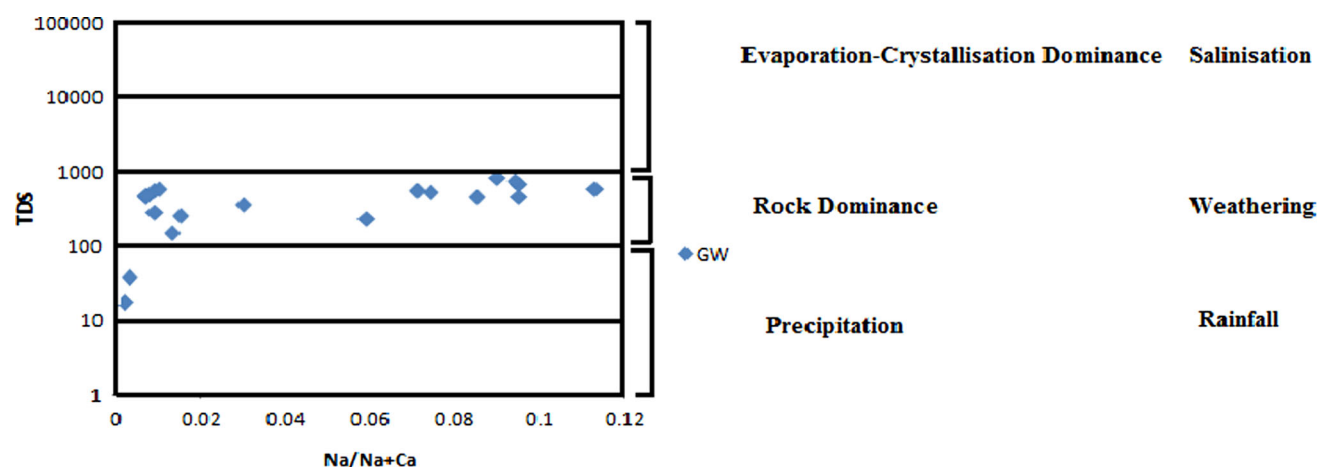
The absence of evaporite settings in the soil zone could be a major factor for the generally low chloride values recorded in the study area. The middle Voltaian consists of rocks such as sandstones, siltstones, shales and tuffs which are not rock salts (evaporites). The Cl<sup>-</sup> could be from precipitation.

The strong correlation between Ca<sup>2+</sup> and Mg<sup>2+</sup> and to a lesser extent with HCO<sub>3</sub><sup>-</sup> suggests that the majority of Ca<sup>2+</sup> and Mg<sup>2+</sup> ions in the groundwater in the study area are probably owed to the dissolution of dolomite. Other possible source of Mg<sup>2+</sup> ions in the groundwater could be from natural softening by cation exchange where sodium-rich clay displaces Ca<sup>2+</sup> and Mg<sup>2+</sup> from solution (Ganyaglo et al. 2010).

There is also a weak positive correlation between Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>. This could suggest that although calcite may contribute to the source of ions in the study area, it might be minimal. Weathering of Anorthite and dolomite as well as cation exchange could be possible major contributors to the source of Ca<sup>2+</sup> ions in the study area.

**Table 4** Summary of petrographical analyses (all the rocks collected were siltstones)

Sample ID	Modal composition of major rock mineral (%)					
	Sericite	Clay	Iron Oxide	Muscovite	Quartz	Feldspar
GSS1	2	30	3	5	59	1
GSS2	–	29	3	4	64	–
GSS3	–	31	1	3	64	1
GSS4	4	28	2	–	63	3
GSS5	2	33	2	3	60	–
GSS6	2	32	3	–	59	4
GSS7	1	32	1	2	63	1



**Fig. 2** Gibbs diagram [modified after Gibbs (1970)]

**Table 5** Correlation matrix of different water quality parameters at the study area

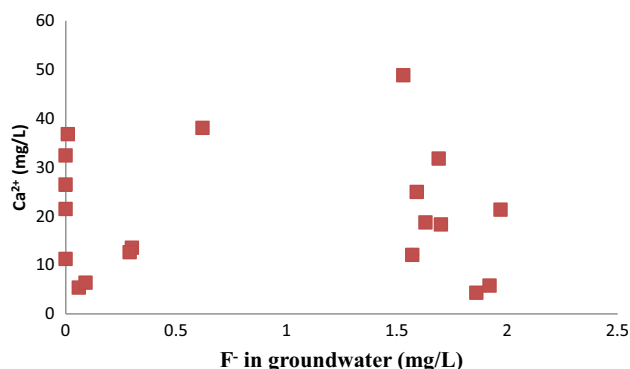
	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>2-</sup>	Fgw	pH	TEMP	EC	TDS
Na <sup>+</sup>	1													
K <sup>+</sup>	-0.259	1												
Ca <sup>2+</sup>	0.107	0.105	1											
Mg <sup>2+</sup>	0.113	0.023	<b>0.732</b>	1										
HCO <sub>3</sub> <sup>-</sup>	<b>0.953</b>	-0.172	0.336	0.351	1									
SO <sub>4</sub> <sup>2-</sup>	0.285	-0.088	-0.063	-0.310	0.157	1								
Cl <sup>-</sup>	0.320	0.003	0.469	0.323	0.339	-0.100	1							
NO <sub>3</sub> <sup>-</sup>	-0.105	-0.208	0.064	0.444	-0.015	-0.241	-0.309	1						
PO <sub>4</sub> <sup>2-</sup>	-0.342	<b>0.654</b>	0.131	-0.065	-0.299	-0.264	0.368	-0.386	1					
Fgw	0.107	0.042	-0.018	-0.243	0.088	-0.080	0.175	-0.483	0.185	1				
pH	0.203	0.450	0.124	0.031	0.255	-0.148	0.308	-0.265	0.315	0.465	1			
TEMP	-0.132	-0.133	-0.127	-0.448	-0.209	0.049	0.200	-0.489	0.078	0.340	0.131	1		
EC	<b>0.735</b>	-0.204	0.503	0.386	<b>0.806</b>	0.310	0.414	-0.269	-0.212	0.271	0.264	-0.099	1	
TDS	<b>0.853</b>	-0.215	0.463	0.352	<b>0.920</b>	0.290	0.337	-0.149	-0.324	0.222	0.202	-0.183	0.932	1

Bold values indicate significance P value ( $P > 0.5$ )

The absence of K-feldspars in rocks in the study area could contribute to the low K<sup>+</sup> levels in the groundwater. Ion exchange in illite may probably be the major process accounting for the K<sup>+</sup> in the groundwater.

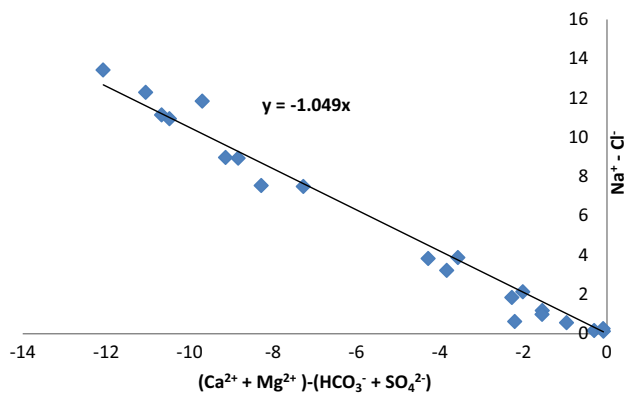
Fluoride in groundwater correlates very weakly and negatively with Ca<sup>2+</sup> (-0.018). Fluoride is readily available in water that has low Ca<sup>2+</sup> and high Na<sup>+</sup> concentrations (Larsen and Widdowson, 1971). F<sup>-</sup> forms strong complexes with other ions, particularly Ca<sup>2+</sup>, Fe<sup>3+</sup>, PO<sub>4</sub><sup>3-</sup> and B(OH)<sub>4</sub><sup>-</sup> in solution. The concentration of F<sup>-</sup> ions in solution is sometimes controlled by the solubility of fluoride; hence, the concentration of F<sup>-</sup> is often inversely proportional to that of Ca<sup>2+</sup>. The absence of calcium in solution therefore catalyzes higher concentrations of F<sup>-</sup> to be stable (Edmunds and Smedley 1996). High fluoride concentrations may therefore be expected in groundwater

from calcium-poor aquifers and in areas where fluoride-bearing minerals are common. Figure 3 shows that the F<sup>-</sup> and Ca<sup>2+</sup> do not have any defined correlation or pattern and



**Fig. 3** A plot of F<sup>-</sup> groundwater against Ca<sup>2+</sup>





**Fig. 4** A plot of  $[\text{Ca}^{2+} + \text{Mg}^{2+} - (\text{HCO}_3^- + \text{SO}_4^{2-})]$  against  $(\text{Na}^+ - \text{Cl}^-)$

as such there could be no concrete conclusion on the possible influence of fluorite in the dissolution of fluoride in the study area. Fluoride is also readily available in areas where fluoride-bearing minerals such as muscovite, hornblende, apatite, and fluor spar are common and these release fluoride into water (Edmunds and Smedley 1996; NAS 1971a). More than 90 % of natural fluoride in soils is bound to clay particles (Lahermo and Backman 2000). Korting (1972) reported that in clay fractions 80–90 % of fluorides are contained in muscovite, illite, and related minerals of the mica group. Fluoride occurs in soil in a variety of minerals and its mobility is determined by the amount of clay minerals present as well as the soil pH (Wong et al. 2003).

Anthropogenic sources of fluoride may include phosphate fertilizers, mine tailings, and landfilled industrial and municipal wastes (EPA 1980a; NAS 1971a). Absence of mining activities and landfills for industrial and municipal wastes in the communities in the study area makes it less likely that the elevated fluoride concentrations in groundwater would result from contamination from such sources. The possible factors for the elevated fluoride concentrations could be phosphate fertilizers, deposition of fluorides by air and from fluoride-bearing minerals. 95 % of the groundwater was sampled from aquifers located within weakly micaceous mudstones and siltstones. Minerals identified from the rocks in the study area include plagioclase feldspars, iron oxide, muscovite and sericite. Sericite is generally from the alteration of muscovite. The Gibbs plot suggests that rock weathering and precipitation are the major hydrogeochemical processes regulating the water chemistry of the study area. This suggests that the elevated fluoride values may be attributed to the weathering of muscovite and sericite. This is similar to the findings of Anim-Gyampo et al. (2012) and Yidana and Yidana (2010), who attribute the sources of fluoride in the Gushegu district and Keta Basin to the presence of sericite and

mineral weathering, respectively. The study area is a sedimentary terrain with much clay contents and this aids in the mobility of the fluoride. Phosphate fertilizers could also contribute to the source of fluoride in groundwater (EPA 1980a) in the study area although it might be minimal. These high  $\text{F}^-$  values have the potential of causing serious health problems such as kidney failure, dental and skeletal fluorosis, reproductive problem and reduction in intelligent quotient of consumers.

The  $\text{NO}_3^-$  concentrations in the study area could originate from organic sources such as animal droppings, domestic sewage or aerobic decomposition of organic matter in the soils as well as the application of nitrate fertilizers. The study area is predominantly a farming community where natural fertilizers such as animal droppings are applied in large quantities on farms in addition to moderate amounts of nitrate-bearing artificial fertilizers. These could be eventually leached into the groundwater system. The low concentration of nitrate recorded in groundwater in the study area could be as a result of the absence of heavy industries which otherwise would have released nitrate-containing effluents.

One possible source of the high bicarbonate in groundwater is the soil zone, by dissociation of carbonic acid ( $\text{H}_2\text{CO}_3$ ) generated by the reaction of  $\text{CO}_2$  with  $\text{H}_2\text{O}$ .  $\text{CO}_2$  may be generated by the decay of organic matter in the soil zone (Ganyaglo et al. 2010). The intense farming activities in the study area generate a lot of organic matter. This results in the enrichment of  $\text{CO}_2$  in the soil zone, which is leached to the groundwater zone as  $\text{HCO}_3^-$ . Carbon dioxide in the atmosphere could also contribute to the high  $\text{HCO}_3^-$  values in the area.

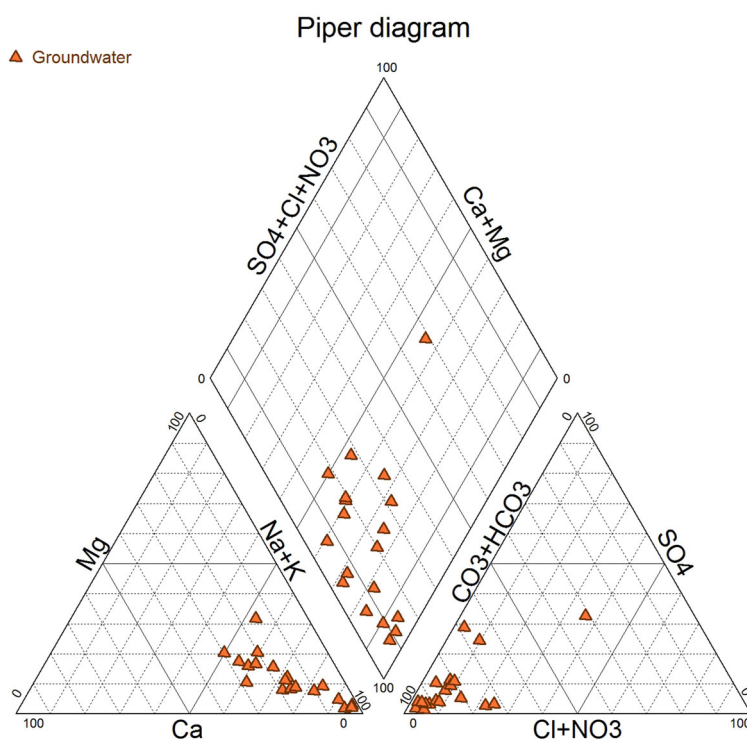
### Cation exchange

To determine whether cation exchange plays a major role in the hydrochemistry of groundwater from the study area, a scatter plot of  $[(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})]$  in meq/L against  $(\text{Na}^+ - \text{Cl}^-)$  in meq/L is carried out (Fig. 4). According to Jankowski et al. (1998), if cation exchange is a significant process in the area, there should be a linear relationship between the two set of parameters, with a slope of  $-1$ . Similarly, the plot displays a linear relationship with a slope of approximately  $-1$  (thus  $-1.049$ ), indicating that cation exchange is a significant process in the study area.

### Water types in the study area

Groundwater is generally classified into facies depending on the dominant ions present. Figure 5 shows the Piper (1944) trilinear plot of the groundwater in the study area. Two main hydrochemical water types are identified. These

**Fig. 5** Piper (1944) trilinear plot



are Na–HCO<sub>3</sub> (water type I) and Na–Ca–Mg–HCO<sub>3</sub> (water type II). The major water type identified in the area is the Na–HCO<sub>3</sub> and occupies about 63 % of the water samples in the study area. The origin and evolution of Na–HCO<sub>3</sub> groundwater have been explained by many authors by combining various hydrogeochemical processes and water–rock interaction reactions. These reactions include (i) the dissolution of CaCO<sub>3</sub> in the presence of biogenic CO<sub>2</sub> accompanied by Ca for Na ion exchange; (ii) a succession of three different reactions: reaction of Na with kaolinite to form Na–beidellite and H<sup>+</sup>, followed by dissolution of CaMg(CO<sub>3</sub>)<sub>2</sub> by H<sup>+</sup> which releases CaMg and HCO<sub>3</sub>, then exchange of Ca and Mg for Na, (iii) the dissolution of dawsonite (NaAlCO<sub>3</sub>(OH)<sub>2</sub> (Maduabuchi et al. 2006). The commonest minerals in the rocks in the study area have been described earlier in this text. The primary source of most sodium in natural water is from the release of soluble products during the weathering of the plagioclase feldspars (Davis and DeWiest 1966; Chapelle and Knobel 1983; Meisler et al. 1984). It may be possible that the plagioclase feldspars (particularly Albite) decomposed to release Na<sup>+</sup> in the groundwater. Acheampong and Hess (1998) illustrated the dissolution of plagioclase feldspar to release Na<sup>+</sup>. The bicarbonate in the groundwater could be from some carbonate mineral dissolution in the aquifer(s) in the area.

The other water type (minor water) is Na–Ca–Mg–HCO<sub>3</sub> (water type II) and referred to as the mixed water. In

this type of water, no particular cation dominates and the dominant anion is HCO<sub>3</sub>. Breakdown of plagioclase feldspars, dolomite as well as the HCO<sub>3</sub> in the soil zone could be responsible for such mixing of waters.

### Isotopes

The stable isotope content of groundwater in the study area is presented in Table 6.

Figure 6 is a plot of δ<sup>18</sup>O against δ<sup>2</sup>H to determine the origin of groundwater in the Gushegu district. The Global Meteoric Water Line (GMWL) determined by Craig (1961) and defined by Eq. 1;

$$\delta^2\text{H} = 8\delta^{18}\text{O} + 10 \quad (1)$$

where δ is the isotopic enrichment parameter, O and H are heavy isotopes of oxygen and hydrogen, respectively, inserted. However, the GMWL is a global line of best fit and as such, may not reflect the local condition. Akiti's (1987) Local Meteoric Water Line (LMWL) defined by Eq. 2 as;

$$\delta^2\text{H} = 7.86\delta^{18}\text{O} + 13.61 \quad (2)$$

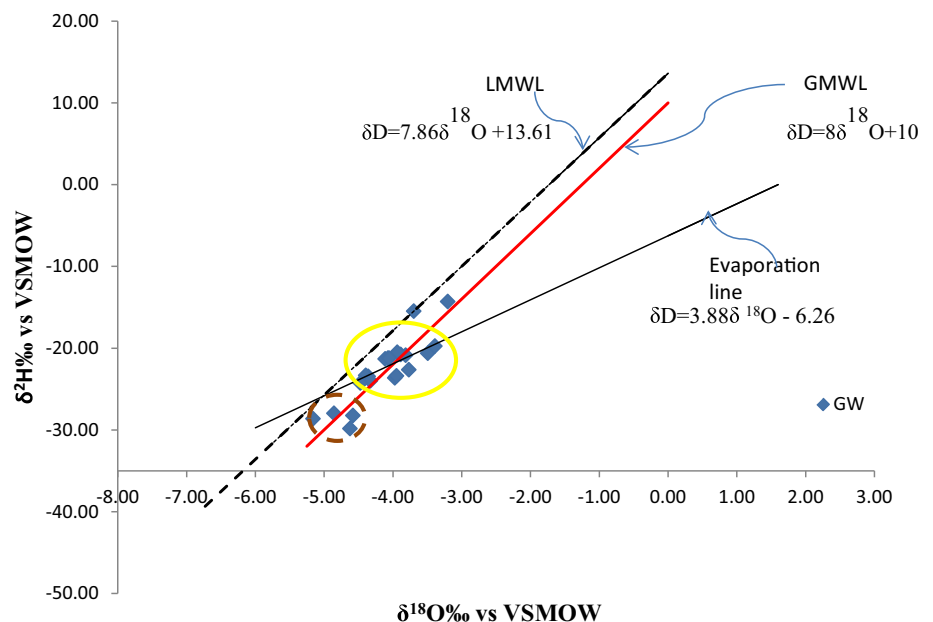
is therefore inserted to serve as a reference for the LMWL in Ghana. This serves as the basis for discussion on the possible origin of groundwaters in the Gushegu District.

The groundwater shows considerable variation in isotopic content. The stable isotope of the groundwater

**Table 6** Stable isotopes content of groundwater in the Gushegu district

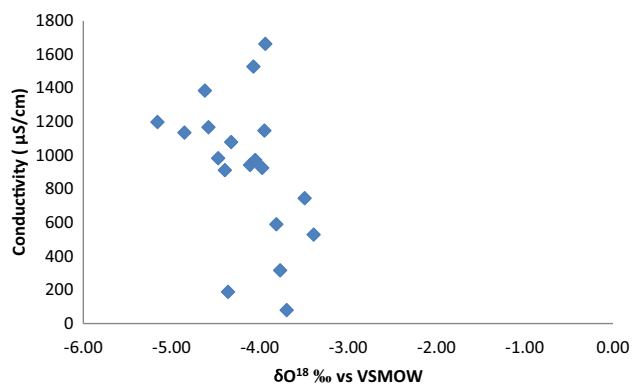
Locality	Sample id	$\delta^{18}\text{O}$ ‰ vs. V-SMOW	$\delta\text{D}$ ‰ vs. V-SMOW
Tinguri	GW1	-4.62	-29.83
Salaa B1	GW2	-3.77	-22.63
Salaa HD2	GW3	-3.81	-20.86
Mongoli B1	GW4	-5.16	-28.65
Mongoli B2	GW5	-4.85	-27.98
Nasingbung B1	GW6	-4.36	-23.44
Nasingbung B2	GW7	-4.58	-28.23
Pumo B1	GW8	-3.97	-23.64
Pumo B2	GW9	-3.49	-20.62
Pumo B3	GW10	-4.40	-23.33
Makendaya	GW11	-3.94	-20.50
Gindigiri	GW12	-3.69	-15.48
World vision guest house	GW13	-4.07	-21.23
Gushegu agric office	GW14	-4.11	-21.32
World vision office	GW15	-4.32	-24.01
Gushegu town	GW16	-4.47	-24.29
Gushegu D/A	GW17	-3.39	-19.75
Gushegu sec. school B1	GW18	-3.95	-23.40
Gushegu sec. school B2	GW19	-4.05	-21.23
Mean		-4.10	-22.64
Minimum		-5.16	-29.83
Maximum		-3.20	-14.32

**Fig. 6** A graph of  $\delta^2\text{H}$  against  $\delta^{18}\text{O}$  of groundwater in the Gushegu District



ranges from  $-5.16$  to  $-3.39$  ‰ and  $-29.83$  to  $-15.48$  ‰ for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , respectively (Table 6). Most of the sample plot on or near the GMWL (circled yellow). Craig (1961), Davis (2002), Domenico and Schwartz (1998) suggest that water with an isotopic composition that falls along the GMWL may probably originate from the

atmosphere and is relatively unaffected by isotopic processes. This suggests that the groundwater is likely to be recharged from local precipitation and could be fresh water. The high vegetation canopy could also turn to serve as a shade and thus reduces evaporation rate in the study area.



**Fig. 7** A graph of conductivity against  $\delta^{18}\text{O}$

Tinguri ( $-4.62\text{‰}$  for  $\delta^{18}\text{O}$  and  $-29.83\text{‰}$  for  $\delta^2\text{H}$ ), Mongoli B1 ( $-5.16\text{‰}$  for  $\delta^{18}\text{O}$  and  $-28.65\text{‰}$ ), Mongoli B2 ( $-4.85\text{‰}$  for  $\delta^{18}\text{O}$  and  $-27.98\text{‰}$  for  $\delta^2\text{H}$ ) and Nas- ingbung B2 ( $-4.58\text{‰}$   $\delta^{18}\text{O}$  and  $-28.23\text{‰}$  for  $\delta^2\text{H}$ ) are relatively more depleted than the other groundwaters, which could suggest that they are relatively old waters. However, a plot of conductivity against  $\delta^{18}\text{O}$  (Fig. 7) shows that the ions are mainly as a result of dissolution. This is in agreement with the Gibbs plot which suggests that the sources of ions in the study area are mainly due to precipitation and dissolution.

A few of the groundwater samples, however, show considerable enrichment including the hand-dug wells. This might be an indication that either rainfall might have suffered some level of evaporation before reaching the groundwater table or groundwater might not have been recharged from the local precipitation but from distant sources as was suggested by Pelig-Ba (2009). The hand-dug wells are open ones and are therefore exposed to direct impact of sunshine and subsequent evaporation.

## Conclusions

Results of groundwater sample analyses in the Gushegu district shows that the pH is weakly acidic to slightly alkaline. The other physicochemical parameters of groundwater in the Gushegu District suggest that they are generally not potable due to their  $\text{F}^-$ , EC and  $\text{HCO}_3^-$  values. 64 and 53 % of the waters recorded levels above the WHO (1996) values of 700 and 380 mg/L for EC and  $\text{HCO}_3^-$ , respectively. Furthermore, the high fluoride contents recorded in about 53 % of the groundwater samples do not make waters from such sources potable. These high values could pose a significant threat to the health of inhabitants of the study area and would require prior treatment of the groundwater before being used for drinking. The study also reveals that the sources of ions in the

waters in the study area are mainly mineral weathering and precipitation. Two water types are identified in the Gushegu District. These are  $\text{Na}-\text{HCO}_3^-$  and  $\text{Na}-\text{Ca}-\text{Mg}-\text{HCO}_3^-$  water types. The former happens to be fresh water and the major water type in the study area. Measurement of environmental isotopes of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  reveals that most of the groundwater in the Gushegu District is of meteoric origin with some few showing considerable enrichment. However, the absence of rainfall data does not allow for conclusive interpretation of the isotope results.

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