Hydrogeochemical framework of groundwater within the Asutifi-North District of the Brong-Ahafo Region, Ghana

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Abstract

Hydrogeochemical processes responsible for groundwater composition within the Asutifi-North district were assessed. The aim was to delineate the factors influencing groundwater within the district. Results show that the pH values of groundwater within the district are moderately acidic to neutral and ranged from 4.4 to 7.5 with a mean value and standard deviation of 6.1 ± 0.7 pH units. 67.4% of groundwater is acidic (pH 4–6.5) due principally to the influence of aquifer materials on the chemistry of groundwater. Acid mine drainage investigations in groundwater within the district shows that, when exposed, sulphides such as pyrites (FeS_2) and arsenopyrite (FeAsS) react with water and oxygen to principally produce $\text{Fe}(\text{OH})_3$. The major ion concentrations are within the WHO (2004) Guideline values for drinking water. The relative abundance of cations and anions in groundwater within the district is in the order of: $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$, respectively. The study further shows that, albite/anorthite-(plagioclase) and calcite/dolomite(carbonates) dissolution as well as ion-exchange reactions may have contributed significantly to major ion concentrations in groundwater within the district. Hydrochemical facies using Piper trilinear diagrams delineated two major water types, the Ca–Mg– HCO_3 and Na–Cl water types, with Ca–Mg–Cl, Ca–Mg– SO_4 –Cl and Na–K– HCO_3 as minor water types. Using principal component analysis (PCA), three (3) main principal components accounting for 73.1% of the total variance with eigenvalues > 1 were extracted. PCA delineated the main natural processes through which groundwater within the district acquires its chemical characteristics, the incongruent dissolution of silicate/aluminosilicates and the prevalence of pollution principally from the application of inorganic fertilizers such as nitrates and ammonia via agricultural activities within the district.

Keywords Hydrogeochemical processes · Groundwater pollution · Principal component analyses (PCA) · Asutifi-North District · Ghana

Introduction

Groundwater is an integral part within the framework of potable water supply to most communities and provides the water needs of millions of people who hitherto were without access to potable water across the world. According to the statistics, nearly one-third of the world's population depends on groundwater for drinking (Tay 2015). Notwithstanding, nearly 30% of freshwater in the world is stored as groundwater with almost 97% of all freshwater readily available for use (Tay 2015). The percentage freshwater (30%) availability, however, is threatened by natural biochemical and

geochemical processes within aquifers as well as anthropogenic activities. The monitoring of these threats is therefore critical to ensure the protection of available freshwater for human use throughout the world. Within the framework of the monitoring of available freshwater, groundwater monitoring plays a critical role. Knowledge of groundwater chemistry is not only critical for ascertaining the source of groundwater contamination but also the identification and characterization of the factors controlling the basic hydrochemistry in a region (Surinaidu 2016). The application of geochemical footprint in the evaluation of various hydrogeochemical processes such as water–rock interaction, identification of recharge area, ion-exchange processes along groundwater flow paths, mechanisms controlling the chemistry of groundwater in a region, salinization of groundwaters in coastal aquifers and the stability of silicate/carbonate minerals and their possible secondary weathering products

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has been extensively studied (Tardy 1971; Jankowski et al. 1998; Andre et al. 2005; Singh et al. 2008; Hussien et al. 2016; Surinaidu et al. 2016; Tay et al. 2017; Shakya et al. 2019; Mengistu et al. 2019). Classification and source identification of dissolved ions in groundwater have the advantage of providing useful information for policy makers towards sustainable management of these vital resources. The quality of groundwater is influenced by physical, chemical and biological constituents and also depends on the composition of recharge water, water–rock–soil interaction in the unsaturated zone, residence time as well as geochemical and biochemical reactions that take place within the aquifer (Appelo and Postma 1999).

Literature indicates that the chemical composition of groundwater is influenced by different factors (Appelo and Postma 1999). Groundwater system in every region is characterized by a distinct chemistry owing to the chemical changes in meteoric water recharging its aquifer system (Hem 1991). According to Hounslow (1995), Andre et al. (2005), variations in the chemical quality of meteoric water are determined by factors such as the geologic constituents, composition of infiltrating rainwater, mineralogical constitution of the aquifer, duration of water–soil–rock interaction, dissolution and precipitation of mineral species and anthropogenic influence. Compositional relationships amongst dissolved species in groundwater can reveal the origin of solutes and the hydrogeochemical processes that produced the observed water chemistry (Jalali 2007; Singh et al. 2008). Assessment of the origin of the chemical constituents of groundwater may also reveal the type of chemical composition of groundwater and its subsurface environment in natural conditions (Shakya et al. 2019). The chemical composition type may represent recent freshwater infiltration which is characterized by Ca–Mg–HCO₃ and Ca–HCO₃ types or ion-exchange reactions characterized by Na–HCO₃ type or relatively longer groundwater residence times during which interaction between the rocks and water is sustained for a longer period of time resulting in greater degree of interaction which leaches ions into groundwater/influence of local rain characterized by Na–Cl type (Shakya et al. 2019). The application of geochemical footprint in the characterization of hydrochemistry of groundwater as well as the identification of the geochemical processes that governs the water chemistry within a region is therefore crucial for the explicit understanding and knowledge broadening within the framework of sustainable management of water resources.

The effectiveness of multivariate statistical techniques in classifying and distinguishing intricate hydrochemical changes and the hidden processes that control the hydrochemical dynamics in aquifers have been extensively studied previously (Machiwal et al. 2015; Surinaidu 2016; Tay et al. 2017; Das

et al. 2019). This technique has been employed with significant success as a tool in the study of groundwater geochemistry. It has been established that multivariate statistical techniques offer an important tool for the interpretation of complex water quality datasets, unravelling of hidden pollution sources and the factors (either natural or anthropogenic) responsible for these sources (Das et al. 2019). The proficiency of PCA model over the theoretical data is rooted in its ability to further expose hidden inter-variable relationships and allows the use of virtually limitless number of variables with precision. By means of raw data as variable inputs, the avoidance of errors arising from close number systems within the theoretical data is guaranteed (Tay 2015). Additionally, since each water quality parameter is treated as an independent variable, the masking effect of chemically related water quality parameter that are often grouped together is avoided (Tay 2015). The PCA model has been used to identify with precision patterns in theoretical data set of high dimension and expressing the data in such a manner that it accurately emphasizes their similarities and differences while simultaneously maintaining the characteristics of the data set that contribute most to its variance (Tay 2015). The PCA model accurately transforms observed variables within the theoretical data into a new set of uncorrelated variables and subsequently organizes them in decreasing order of importance with precision. The PCA model further shrinks the dimensionality of the data set by elucidating the association amongst large number of variables in terms of a smaller number of underlying factors without losing important information with precision (Tay 2015). Thus, the application of multivariate statistical technique assists in the interpretation of multifaceted data matrices to better understand the water quality as well as identify the possible factors that influence the water chemistry in a region.

It is worthy to note that scientific data on the chemistry of groundwater within the Asutifi-North district to allow for the proper management and development of groundwater within the district using conventional hydrogeochemical and statistical tool is either non-existent or very limited. Characterization of the water quality in this region using these tools within the framework of sustainable management is thus imperative.

The objective of this paper therefore was to assess and characterize the water quality of the Asutifi-North district using hydrogeochemical and statistical tools in order to delineate the processes that control groundwater chemistry within the district and assist the local communities who depend on these water resources as well as the managers to sustainably manage these resources.

Materials and methods

Study area

Location and physical setting

The study area lies within the Sefwi Gold Belt in the Asutifi-North district between Latitudes 6° 40' N and 7° 15' N and Longitudes 2° 15' W and 2° 45' W at South-Western corridor of Brong-Ahafo Region (Fig. 1).

Topography and drainage

The topography of the study area is generally characterized by undulating landscape. It is characterized by outcrop of metamorphosed rocks in some communities such as Goaso, Konkreteso, Georgekrom. The major rivers and other waterbodies which drain the area includes River Tano and its tributaries such as Goaso, Ntotro, Akentansu, Subika, Kwamiasua, Samansua, Asundua and Subri. Other tributaries include Amoma, Kankam, Benu, Yaya and Bisi. The area lies within the middle belt of Ghana with topography ranging between 200 and 467 m above mean sea level.

Climate and vegetation

The wet semi-equatorial climatic condition prevails in and around the settlement. Annual rainfall ranges between 1400 and 1750 mm and a mean annual temperature of about

26.6 °C (Dickson and Benneh 2004). The mean monthly temperature ranges between 23 °C in August and 33 °C in March and April (Dickson and Benneh 2004). The relative humidity varies between 75 and 80% during the wet season and below 70% during the dry season (Dickson and Benneh 2004). The vegetation of the study area is predominantly moist–semi deciduous forest. Tree crops such as cocoa and citrus thrive well in this zone (Dickson and Benneh 2004).

Hydrogeological characteristics

The area is underlain mainly by Birimian Supergroup and forms part of the Paleoproterozoic supracrustal and intrusive rocks, which formed between 2195 and 2072 Ma. It exhibits a characteristic pattern of NE-trending with parallel volcanic belts and intervening sedimentary basin in the Sefwi Belt terrain (Fig. 2). The volcanic rocks in these belts are mostly intruded by synvolcanic granitoid plutons mainly granodiorite. These rocks represent tectonically stacked sequence of volcanic chain with low-grade metamorphosed, tightly to isoclinically folded sediments comprising greywackes, granitoids and granodiorites depending on relative abundance. The other major rock types in the terrain include phyllite, pyroclastic rocks and amphibolite, schist, slate, greywacke, tuff and lava (Kesse 1985). These rocks are strongly folded, foliated and jointed with associated intense weathering along fractures and other weak zones such as bedding and cleavage planes, which facilitate groundwater development. Where they crop out or are near the surface, considerable water may percolate through them. Boreholes tapping the Birimian

Fig. 1 Location and land-use map of Asutifi-North district

Fig. 3 Map of the study area (insert map of Ghana) showing sampling communities

(SiO_2) by the formation of molybdosilicate in the molybdate yellow method and spectrophotometric determination at 690 nm; chloride (Cl^-) by argentometric titration and Iron (Fe^{2+}) by Agilent 240FS atomic absorption spectrometer by direct aspiration of water samples into an air acetylene flame. As a basis for scrutinizing analytical results, an ionic balance was calculated for each chemical sample. Results with ionic balance greater than 5% were rejected in agreement with international standards (Tay et al. 2017). Charge balances (CB) were calculated based on Tay et al. (2017) as in Eq. (1):

$$\text{CB} = \left[\left(\sum z \text{Mc} - \sum z \text{Ma} \right) / \left(\sum z \text{Mc} + \sum z \text{Ma} \right) \right] * 100 \quad (1)$$

where z is the ionic charge and M the molality, and the subscripts, a and c symbolizes anions and cations respectively.

Data analysis

The hydrochemical data were analysed using SPSS 16.0 software package. Bivariate plots used for the determination of the sources of major ions were drawn using Microsoft Excel 2013. The stability diagrams of albite and anorthite and their possible secondary weathering products were drawn with the assumption that all aluminium is preserved in the weathering products (Appelo and Postma 1999). End-member compositions were also assumed using equilibrium relationships of Tardy (1971) for standard temperature (25 °C) and pressure (1 atmosphere) which principally reflects conditions in the groundwater. Computations of constituents' activities were done using Phreeqc for Windows Version 2.8.01 (Appelo and Postma 1999). AquaChem 4.0 was used to extract the Piper trilinear plot for the delineation of the water types. Principal component analysis (PCA)

was performed using Varimax with Kaiser normalization. An eigenvalue provides a measure of the significance of the factor with, the factor having the highest eigenvalue as the most significant. Eigenvalues of 1.0 or greater are considered significant (Tay et al. 2017). Corresponding to absolute loading values of > 0.75 , $0.75-0.50$, $0.50-0.30$, factor loadings are classified as 'strong', 'moderate' and 'weak' respectively (Tay et al. 2017).

Results and discussions

Hydrochemistry

Table 1 presents the statistical summary of the hydrochemical data for groundwater within the district, while Table 2 presents the classification of groundwater based on hardness values. Table 3 presents the component matrix of the main physico-chemical parameters, while Table 4 presents the total variance in the hydrochemical data.

Groundwater temperatures within the Asutifi-North district are characteristics of tropical waters and ranged $25.8-32.9$ °C with mean and standard deviation value of 28.1 ± 1.9 °C. According to Stumm and Morgan (1981), these values are outside the natural background levels of $22.0-29.0$ °C for waters in the tropics.

The pH values of boreholes are moderately acidic to neutral and ranged $4.4-7.5$ with a mean value and standard

Table 2 Classification of groundwater based on hardness values

Hardness (mgL ⁻¹ as CaCO ₃)	Water classification	Number of groundwater	Percentage (%)
0–75	Soft	16	34.8
75–50	Moderately hard	6	13.0
150–300	Hard	19	41.3
> 300	Very hard	5	10.9
Total	–	46	100

After Todd (1980)

deviation of 6.1 ± 0.7 pH units. Based on Hounslow (1995), 67.4% of groundwater are moderately acidic (pH 4–6.5). The moderately acidic characteristics of groundwater within the district may be due to the influence of aquifer materials on the chemistry of groundwater. The presence of sulphides and carbonaceous matter within the ore formations according to the geology of the catchment area suggests that natural geochemical and biochemical oxidation of these rocks may occur when in contact with oxygen gas containing water, resulting in increased hydrogen ion activity in the waters with which they are in contact. According to Tay (2015) when exposed, sulphides such as pyrites (FeS₂), arsenopyrite (FeAsS) and chalcopyrite (CuFeS₂) react with water and oxygen to produce sulphuric acid (H₂SO₄) mainly ensuing to the production of acid mine drainage. The mechanism involved in the acid mine drainage production can be explained as follows; pyrite is oxidized by oxygen

Table 1 Statistical summary of water quality parameters within Asutifi-North district

Parameter	Minimum	Maximum	Mean	SD
Temperature	25.8	32.9	28.1	1.9
pH	4.4	7.5	6.1	0.7
EC	26.0	1377.0	445.4	333.6
TDS	14.3	757.4	244.9	183.5
Total hardness	8.8	492.0	159.8	123.8
Alkalinity	8.0	336.0	118.1	88.8
Ca ²⁺	2.4	107.0	28.7	27.5
Mg ²⁺	0.6	65.4	18.1	16.3
Na ⁺	0.8	60.0	21.2	16.5
K ⁺	0.09	5.7	1.9	1.4
Cl ⁻	7.9	228.0	32.8	45.2
HCO ₃ ⁻	9.8	434.0	147.8	114.3
SO ₄ ²⁻	0.3	117.0	26.2	29.3
PO ₄ -P	0.02	0.7	0.19	0.15
NO ₃ -N	0.005	3.8	0.4	0.2
SiO ₂	0.29	1.7	0.9	0.4
NH ₄ -N	0.04	0.6	0.3	0.2
Fe ²⁺	0.005	1.98	0.27	0.15

All parameters are in mg/L, except, Temperature (°C), EC (μS/cm)

Table 3 Component matrix of the main physico-chemical parameters

	Component		
	1	2	3
<i>Chemical Parameter</i>			
TDS	0.967	0.102	-0.115
EC	0.967	0.102	-0.115
Total hardness	0.952	0.042	-0.082
Na ⁺	0.812	0.154	-0.097
Ca ²⁺	0.811	0.286	0.204
Mg ²⁺	0.772	-0.178	-0.280
K ⁺	0.770	0.242	0.257
SO ₄ ²⁻	0.770	0.235	0.119
pH	0.734	-0.538	-0.005
HCO ₃ ⁻	0.686	-0.466	-0.224
Cl ⁻	0.663	0.636	0.047
SiO ₂	0.510	-0.433	0.432
NO ₃ -N	-0.451	0.477	-0.392
NH ₄ -N	0.192	-0.470	-0.111
PO ₄ -P	-0.136	0.035	0.809

Extraction method: principal component analysis

Table 4 Total variance explained

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	7.843	52.290	52.290	7.843	52.290	52.290	6.401	42.671	42.671
2	1.821	12.138	64.428	1.821	12.138	64.428	3.247	21.647	64.318
3	1.303	8.687	73.115	1.303	8.687	73.115	1.320	8.797	73.115
4	0.974	6.490	79.605						
5	0.776	5.174	84.779						
6	0.572	3.812	88.591						
7	0.473	3.150	91.742						
8	0.356	2.372	94.113						
9	0.307	2.049	96.162						
10	0.267	1.778	97.940						
11	0.169	1.125	99.065						
12	0.081	0.539	99.603						
13	0.044	0.292	99.895						
14	0.016	0.105	100.000						
15	4.457E-9	2.971E-8	100.000						

Extraction method: principal component analysis

in the presence of water and ferrous iron to produce Fe^{2+} , SO_4^{2-} and H^+ as presented in reaction Eq. (2) (Tay 2015):

The ferrous ion (Fe^{2+}) produced in reaction Eq. (2) is then oxidized to ferric ion (Fe^{3+}) in the presence of *Thiobacillus Ferrooxidans* as a catalyst in a relatively slow reaction as depicted by Eq. (3):

According to Tay (2015), the reaction Eq. (3) is the major rate-determining step of acid mine drainage formation. Any further development of the acid drainage process is dependent on the pH of the water of interest. If the $\text{pH} > 3$ as is the case of groundwater within the Asutifi-North district where the pH range was 4.4–7.5; then, $\text{Fe}(\text{OH})_3$ is principally precipitated as presented in reaction Eq. (4):

Thus, acid mine drainage reactions in groundwater within the Asutifi-North district principally produces $\text{Fe}(\text{OH})_3$. It is noteworthy to indicate that the oxidation of arsenopyrite (FeAsS) and other sulphide minerals by oxygen through proton production undergoes analogous reactions (Tay 2015). Additionally, the moderately acidic characteristics coupled with the low SO_4^{2-} concentration and low conductivity of most of the shallow groundwater suggests that acidity could result from the production of carbonic acid from atmospheric CO_2 during rainfall or through the solution of

soil-generated CO_2 and dissolved organic acids such as fulvic and humic acids (Langmuir 1997).

Groundwater within the district was characteristically low to highly mineralized as the electrical conductivity ranged 26.0–1377.0 $\mu\text{S}/\text{cm}$, with a mean value of $445.4 \pm 336.0 \mu\text{S}/\text{cm}$. The electrical conductivity values shows that 52.2% of groundwater within the district can be classified as fresh waters ($\text{EC} < 500 \mu\text{S}/\text{cm}$) according to the classification by Hounslow (1995). Total dissolved solids (TDS) ranged 14.3–757 mg/L with mean and standard deviation of 224.9 (± 183.5) mg/L. According to Hounslow (1995), groundwater within the district perhaps undergoes silicate weathering as 95.6% of groundwater had TDS values < 500 mg/L. The high standard deviation in TDS and EC reflects the spatial variability in ionic concentrations in groundwater within the district. The large spatial differences in TDS values are perhaps due to lithological variations in the weathering of anorthite and albite present in the rocks and/or local impact of anthropogenic activities within the district. However, groundwater within the district is generally soft to moderately hard. Hardness values ranged 8.8–492.0 mg/L with a mean value and standard deviation of 159.8 (± 123.8) mg/L. Total hardness is due to Ca^{2+} and Mg^{2+} in water. The high standard deviation in total hardness may be due to spatial variability in Ca^{2+} and Mg^{2+} concentrations in groundwater within the district. Todd (1980) classified water hardness into four categories as soft, moderately hard, hard and very hard. Table 2 presents the different classifications of water hardness. Out of the 46 data points, 34.8% are soft, 13.0% are moderately hard, 41.3% are hard and 10.9% are very hard. Based on this classification, only 47.8% of the

groundwater in the district can be said to be potable for drinking and domestic purposes.

Groundwater alkalinity within the district ranged 8.0–336.0 mg/L with a mean and standard deviation of 118.1 ± 88.8 mg/L. The chemical constituents generally have low concentrations (Table 1) and are within the WHO (2004) Guideline values. The boxplot of the major ion concentrations in groundwater within the district is presented in Fig. 4. The error bars in Fig. 4 depicts the spatial variability in ionic concentrations in groundwater within the district. From Fig. 4, HCO_3^- is the dominant anion in groundwater within the district. Tay et al. 2017 showed that for groundwaters with HCO_3^- as dominant anions, groundwater composition takes place at outcrops. Compared with other cations, the concentration of Ca^{2+} is relatively high. The relative abundance of cations and anions in groundwater within the district is in the order of: $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ respectively.

NO_3-N in groundwater within the district ranged 0.005–3.77 mg/L, with a mean and standard deviation value of 0.43 ± 0.2 . NH_4-N in groundwater within the district ranged 0.04–0.62 mg/L, with a mean and standard deviation value of 0.3 ± 0.2 . Nitrate is a significant pollutant found in the environment which is a derivative of atmospheric precipitation, human and animal excreta, agricultural fertilizers, biological fixation and nitrification of organic N and NH_4 (Tiwari 2014). NO_3-N concentrations in groundwater within the district is within the WHO guideline value of 10 mg/l for drinking water. This could be due to the low levels of anthropogenic activities and local precipitation within the district. PO_4-P in groundwater within the district ranged 0.02–0.7 mg/L, with a mean and standard deviation value of 0.19 ± 0.15 . SiO_2 in groundwater within the district ranged 0.29–1.7 mg/L, with a mean and standard deviation value of 0.9 ± 0.4 .

Gibbs (1970) has shown that generally, the chemistry of water is controlled by the rate of evaporation, chemical compositions of the rocks (rock weathering) and chemical composition of rainwater (precipitation). Figure 5 presents the scatter plot of TDS (mg/L) vs. $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$

(meq/L) based on Gibbs (1970) showing the mechanisms controlling groundwater chemistry within the Asutifi-North district. Figure 5 shows that rock dominance weathering and precipitation dominance contribute to the hydrogeochemical processes responsible for the chemical evolution of groundwater within the district. According to Hounslow (1995), in environments where the pH is low, it is usually the result of weak acids such as carbonic acid resulting from precipitation or dissolved organic acids derived from decaying organic matter. Consistent with Hounslow (1995), some of the groundwater have moderately low pHs. Thus, the chemistry of their waters may be controlled by precipitation (Fig. 5). Das et al. (2019), in their assessment of groundwater in the Birbhum District West Bengal, India, using Gibbs diagram, showed that the mechanism controlling groundwater in the district was the combination of rock weathering and resultant mixing of minerals. Hussien and Faiyad (2016) employed the Gibbs diagram to determine the mechanism that controls the groundwater of UmErdhuma–Tayarat aquifer situated in a region where dry and semiarid climatic conditions are dominant. The scientists reported that evaporation–crystallization processes significantly control the major ion chemistry of groundwater perhaps due to dry and semiarid climatic conditions. A study

Fig. 5 Scatter plot of TDS (mg/L) against $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ (meq/L) showing rock weathering and precipitation dominances

Fig. 4 Boxplot of major ions in groundwater within the Asutifi-North district

on characterization of recharge mechanism and sources of groundwater salinization in Ras Jbel Coastal Aquifer, Northeast Tunisia, conducted by Abidi et.al. (2017) also employed the Gibbs diagram to investigate the mechanism controlling groundwater in the region. The study showed that there was a combination of rock weathering (weathering of carbonate minerals) as well as the evaporation–crystallization dominances significantly controlling the major ion chemistry of the groundwaters in the Ras Jbel Coastal Aquifer.

Sources of major ions

According to Hounslow (1995), for groundwater with major ion ratios of $\text{Na}^+ / (\text{Na}^+ + \text{Cl}^-) > 0.5$, the origin of sodium is either albite or ion-exchange. Results shows that 66.6% of the groundwater had $\text{Na}^+ / (\text{Na}^+ + \text{Cl}^-)$ ratios > 0.5 , suggesting either albite weathering or ion-exchange reactions as sources of sodium in groundwater within the district. According to Hounslow (1995), in a plot of Na^+ vs. Cl^- , groundwater plotting close to the 1:1 line suggest sodium source from sea aerosol while groundwater plotting above the 1:1 line suggests ion-exchange and groundwater plotting below the 1:1 line suggests reverse ion-exchange. Results from this study shows that majority of groundwater plotted either close to or above the 1:1 line (Fig. 6), suggesting sodium source from either sea aerosol spray or sodium source other than halite; probably, albite (plagioclase) weathering or ion-exchange is partly responsible for Na^+ in groundwater within the district. However, the district is not close to the coast; therefore, sodium source from sea aerosol spray is also unlikely. Thus, albite (plagioclase) weathering or ion-exchange may be partly responsible for Na^+ in groundwater within the Asutifi-North district. This result is consistent with Narany et al. (2014) who conducted hydrogeochemical assessment of groundwater within the Amol-Babol Plain in Iran and reported that the groundwater principally showed a $\text{Na} + / \text{Cl}^-$ ratios ≥ 1 and therefore represents silicate weathering

Fig. 6 Plot of Na^+ vs. Cl^- for groundwater within the Asutifi-North district

processes in groundwater within the Amol-Babol plain. Sources of Cl^- in groundwater include both natural and anthropogenic. Atmospheric precipitation, weathering of halite and dissolution of salt deposits are perhaps the major lithogenic or natural sources of Cl^- in groundwater within the district. Anthropogenic sources of Cl^- in groundwater within the district may include animal wastes, chemical fertilizers and leachates from waste dumps.

Datta et al. (1996), Rajmohan and Elango (2004) and Sandow (2009) showed in their studies that waters plotting above the equiline (1:1) in a plot of $(\text{HCO}_3^- + \text{SO}_4^{2-})$ vs. $(\text{Ca}^{2+} + \text{Mg}^{2+})$, shows a dominance of carbonate weathering while waters plotting below the 1:1 line depicts a dominance of silicate weathering. Figure 7 shows that the groundwater plot above and below the 1:1 line suggesting both carbonate and silicate weathering dominance in groundwater within the district. Additionally, according to McLean and Jankowski (2000), in a plot of $(\text{HCO}_3^- + \text{SO}_4^{2-})$ vs. $(\text{Ca}^{2+} + \text{Mg}^{2+})$, a 1:1 relationship would indicate gypsum, anhydrite, calcite and dolomite dissolution as the predominant processes controlling solution composition while, groundwater falling below the 1:1 line depicts ion-exchange, in which case $\text{Ca}^{2+} + \text{Mg}^{2+}$ are depleted with respect to $\text{HCO}_3^- + \text{SO}_4^{2-}$. As shown in Fig. 7, majority of the waters plot close to and on the 1:1 line, while, a few plot above and below the 1:1 line, suggest gypsum, anhydrite, calcite and dolomite dissolution as well as ion-exchange reactions controlling solution composition in groundwater within the district. Approximately, 88.8% of groundwater also shows that, the $\text{Ca}^{2+} / (\text{Ca}^{2+} + \text{SO}_4^{2-})$ equivalent ratios were greater 0.5, suggesting calcium source other than gypsum-carbonates, calcite/dolomite or silicates. Additionally, 77.7% of groundwater had $\text{HCO}_3^- / \text{SiO}_2$ ratios > 10 , suggesting carbonate weathering reactions. Thus, calcite/dolomite, carbonates or silicate dissolution may have contributed significantly to Ca^{2+} and Mg^{2+} concentrations in groundwater within the district. This result is consistent with Narany et al. (2014) who reported that majority (73.6%) of groundwater within

Fig. 7 Plot of $\text{HCO}_3^- + \text{SO}_4^{2-}$ (meq L^{-1}) vs. $\text{Ca} + \text{Mg}$ (meq L^{-1}) for groundwater within the Asutifi-North district

the Amol-Babol Plain in Iran plotted close to the 1:1 line in a plot of $(\text{HCO}_3^- + \text{SO}_4^{2-})$ vs. $(\text{Ca}^{2+} + \text{Mg}^{2+})$, and therefore, an excess of Ca^{2+} and Mg^{2+} over $\text{HCO}_3^- + \text{SO}_4^{2-}$ and attributed it to the dissolution of calcite, dolomite and gypsum. Mohammed and Zineb (2015) also investigated the hydrogeochemical processes in groundwater in Souf Valley of Low Septentrional Sahara in Algeria and reported that carbonate and silicate weathering are the major hydrogeochemical processes that governs the groundwater chemistry within the Souf Valley.

Generally, the dissolution of carbonate minerals such as calcites and dolomites may be represented by Eqs. (5) and (6), respectively (Al-Amry 2008):

According to Al-Amry (2008), the molar proportions of $(\text{Ca}^{2+} + \text{Mg}^{2+})$: (HCO_3^-) should be linear with a slope of 1, if dolomite dissolution takes place in groundwater. The scatter plot of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ vs. (HCO_3^-) in groundwater within the district is presented in Fig. 8. From Fig. 8, the slope is 0.6983 which is close to the expected (i.e. a slope of 1). There suggests a general excess of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ over (HCO_3^-) in groundwater within the district. This is supported by the hydrochemical data as 77.5% of groundwater had ratios of $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^- > 1$. This does not support the general trend predicted by the dolomite dissolution model $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{HCO}_3^- = 1$, and reflects additional sources of Ca^{2+} and Mg^{2+} in groundwater within the district. This suggests the presence of other carbonate minerals within the subsurface.

The incongruent dissolution of albite to produce the secondary mineral products; kaolinite, montmorillonite and/or gibbsite according to Kortatsi (2004) can be presented in Eqs. (7), (8) and (9), respectively:

Fig. 8 Plot of HCO_3^- (meq L^{-1}) vs. $\text{Ca} + \text{Mg}$ (meq L^{-1}) for groundwater within the Asutifi-North district

(After, Tardy 1971)

Fig. 9 The stability of albite and its possible secondary weathering products gibbsite, kaolinite and Na-montmorillonite with respect to groundwater within the Asutifi-North district

The $\text{H}_4\text{SiO}_4/\text{Na}^+$ molar ratios for the dissolution of albite to kaolinite, montmorillonite and gibbsite as presented in Eqs. (7), (8) and (9) are theoretically 2.0, 0.5 and 3.0, respectively (Kortatsi 2004). The calculated $\text{H}_4\text{SiO}_4/\text{Na}^+$ molar ratios for groundwater within the district ranged 0.4–2.7, with a mean value of 1.6. Clearly, the result suggests that weathering processes in which albite is dissolved into kaolinite and Na-montmorillonite with molar ratios of 2.0 and 0.5, respectively, are taking place in groundwater within the district. Mineral stability diagrams have been widely employed to explicitly explain weathering processes involving silicate minerals in order to establish the most stable silicate mineral phases in the hydrochemical assessment of groundwater (Kashiwagi et al. 2006). The stability of albite and its secondary weathering products gibbsite, kaolinite and Na-montmorillonite with respect to groundwater within the district is presented in Fig. 9. All (100%) groundwater plotted in the kaolinite and Na-montmorillonite fields on the stability diagram of albite and its secondary weathering products (Fig. 9). The calculated molar ratios of kaolinite and montmorillonite are consistent with the data plot in Fig. 9. As shown in Table 1, SiO_2 concentrations in groundwater within the district ranged between 0.29 and 1.7 mg/L, with a mean standard deviation value of 0.9 ± 0.4 . This range falls within the general range of SiO_2 concentrations found in natural waters probably reflecting the low solubility of common silicate minerals (Yidana et al. 2012) such as albite and anorthite present in the geology of the district. Additionally, the pH of groundwater typically have minimum effect on the solubility of SiO_2 , except at $\text{pH} > 9.0$ where the solubility of silicates increases speedily (Yidana et al. 2012). From Table 1, the pH of groundwater within the district is less than 9 (i.e. ranged from 4.4 to 7.5 pH units, and a mean value and standard deviation of 6.1 ± 0.7). Thus, according to Yidana et al. (2012), groundwater pH within the Asutifi-North district cannot provide the needed environments for increase in the rate of solubility of silicates. This further

explains the low solubility of SiO_2 in groundwater within the district.

To further ascertain the source of Na^+ in groundwater, Jankowski et al. (1998) hypothesized that waters undergoing ion-exchange involving Na^+ and Ca^{2+} along the groundwater flow path would normally plot along a line whose slope is -1 in a plot of $\text{Na}-\text{Cl}$ (meq L^{-1}) vs. $\text{Ca} + \text{Mg} - \text{HCO}_3 + \text{SO}_4$ (meq L^{-1}) while, waters plotting close to the zero value on the x-axis are not governed by ion-exchange. The plot of $\text{Na}-\text{Cl}$ (meq L^{-1}) vs. $\text{Ca} + \text{Mg} - \text{HCO}_3 + \text{SO}_4$ (meq L^{-1}) for groundwater within the district is presented in Fig. 10. This study shows that the waters plot along a line whose slope is -0.87 (Fig. 10). This slope is closer to -1 than the zero value on the x-axis. This result is also consistent with the plot in Fig. 6 which showed that albite (plagioclase) weathering or ion-exchange may be partly responsible for Na^+ in groundwater within the district. Cation exchange reactions are therefore one of the dominant processes through which Na^+ enters the groundwater system within the district. Thus, cation exchange reactions and albite (plagioclase) dissolution are perhaps the dominant processes through which Na^+ enters the groundwater within the Asutifi-North district. This result is consistent with Sajil Kumar and James (2016) who investigated the hydrogeochemical processes in groundwater in the Coimbatore District, Tamil Nadu, India, and reported a slope of -0.938 in a plot of $\text{Na}-\text{Cl}$ vs. $\text{Ca} + \text{Mg} - \text{HCO}_3 + \text{SO}_4$ due to a correlation between Ca, Mg and Na through ion-exchange processes.

A further source-rock deduction studies using major ion ratios shows that 62.9 % of the groundwater within the district shows $0.2 < (\text{Na}^+ + \text{K}^+ - \text{Cl}^-) / (\text{Na}^+ + \text{K}^+ - \text{Cl}^- + \text{Ca}^{2+}) < 0.8$, suggesting that anorthite (plagioclase) ($\text{Na}_{0.62}\text{Ca}_{0.38}\text{Al}_{1.38}\text{Si}_{2.62}\text{O}_8$) weathering is possible.

The incongruent dissolution of anorthite (plagioclase) with carbon dioxide charged water to produce Na^+ and

Fig. 10 Plot of $\text{Na}-\text{Cl}$ (meq L^{-1}) vs. $\text{Ca} + \text{Mg} - \text{HCO}_3 + \text{SO}_4$ (meq L^{-1}) for groundwater within the Asutifi-North District

(After Tardy 1971)

Fig. 11 The stability of anorthite (plagioclase) and its possible secondary weathering products gibbsite, kaolinite and Ca-montmorillonite with respect to groundwater within the Asutifi-North district

Ca^{2+} according to Kortatsi (2004) can be represented as in Eq. (10):

Notwithstanding, the weathering of anorthite (plagioclase) in Eq. (10) hypothetically has molar ratios for $\text{H}_4\text{SiO}_4/\text{HCO}_3^-$ and $\text{H}_4\text{SiO}_4/\text{Na}^+$ as 0.9 and 2.0 respectively (Kortatsi 2004). Meanwhile, the computed molar ratios for $\text{H}_4\text{SiO}_4/\text{HCO}_3^-$ and $\text{H}_4\text{SiO}_4/\text{Na}^+$ for groundwater within the Asutifi-North district ranged 0.8–2.3 with a mean value of 1.7. The hydrochemical data therefore suggests that anorthite weathering to produce kaolinite and Ca-montmorillonite markedly explain the excess of Na^+ over Cl^- as well as the sources of Ca^{2+} , H_4SiO_4 and HCO_3^- in groundwater within the district. Thus, anorthite (plagioclase) weathering in groundwater within the district contributes to the concentration of Na^+ , Ca^{2+} , H_4SiO_4 and HCO_3^- . This result is consistent with the data plot on the stability diagram of anorthite (plagioclase) and its possible secondary weathering products (Fig. 11) where all data plot in the kaolinite and Ca-montmorillonite due to Ca^{2+} and SiO_2 contents in the groundwater. Literature indicates that in groundwaters hosted by silicate minerals, interaction between the rocks and groundwater results in the leaching of Ca^{2+} and H_4SiO_4 ions into the groundwater system (Yidana et al. 2012). Such interactions result in different products depending on the residence time, the climate and the flow regime (Yidana et al. 2012). Thus kaolinite and Ca-montmorillonite are the most likely secondary minerals from the dissolution of anorthite (plagioclase) in groundwater within the Asutifi-North district.

Schoeller (1965, 1977) proposed two chloro-alkaline indices— CAI_1 and CAI_2 to clearly explain ion-exchange reactions between groundwater and its host environment during residence time. Computation of CAI_1 and CAI_2 indices for groundwater within the district shows that CAI_1 indices ranged -1.9 to 0.8 with a mean value of -0.4 , while CAI_2 indices ranged -0.5 to 0.8 with a mean value of 0.0 . Majority of the computed CAI_1 and CAI_2 indices are negative suggesting an exchange of Mg^{2+} and Ca^{2+} from groundwater within the district with Na^+ and K^+ in the rocks. Thus, the computed chloro-alkaline indices is consistent with the plot of $\text{Na}-\text{Cl}(\text{meq L}^{-1})$ vs. $\text{Ca} + \text{Mg} - \text{HCO}_3 + \text{SO}_4(\text{meq L}^{-1})$ and therefore suggest that cation-exchange reactions are primarily taking place in groundwater within the Asutifi-North district in which case, Ca^{2+} and Mg^{2+} are being exchanged with Na^+ and K^+ in the rocks.

The common sources of HCO_3^- in groundwater within the Asutifi-North district include weathering of silicate and/or aluminosilicate minerals (albite and anorthite), calcite and dolomite. The relatively high proportion of

HCO_3^- compared to other anions indicates the weathering of primary silicate minerals dominated by alkaline earths

(Tiwari, 2014). SO_4^{2-} concentrations in natural water ranges between 2 and 80 mg/L with higher concentrations attributable to the weathering of sulphide minerals or anthropogenic sources such as agricultural effluents (Tiwari 2014). SO_4^{2-} concentrations in groundwater within the district ranged 0.3–117.0 mg/L, with a mean value of 26.2, and this may possibly be due to chemical products such as ammonium sulphate fertilizers via agricultural activities and the weathering of sulphide minerals. The oxidation of sulphides (pyrites and arsenopyrites) via acid mine drainage is also generally expected to be a significant source of SO_4^{2-} in groundwater (Tay 2015). The oxidation reactions is as presented in Eqs. (2), (3) and (4). Traditionally, these reactions produce high SO_4^{2-} concentrations, low pH and $\text{Fe}^{2+}/\text{SO}_4^{2-}$ molar ratios of 0.5 (for the stoichiometry of pyrite oxidation) and 1.0 (for the stoichiometry of arsenopyrite oxidation) (Tay 2015). However, the generally very low concentration of SO_4^{2-} which ranged 0.003–1.22 mmol/L, in addition to the fact that, no groundwater satisfied the $\text{Fe}^{2+}/\text{SO}_4^{2-}$ molar ratio of 0.5 and 1.0 for the stoichiometry of pyrite and arsenopyrite oxidation, respectively, suggests that pyrite and arsenopyrite oxidation processes are not exclusively responsible for the concentration of SO_4^{2-} in groundwater within the district.

Hydrochemical facies

Figure 12 presents the Piper (1944) trilinear plot of the hydrochemical data for the Asutifi-North district. From Fig. 12, majority (68.1%) of the data points clustered towards the Ca–Mg– HCO_3 dominant section (II) indicating water type characterized by temporary hardness. The Ca–Mg– HCO_3 water type denotes vigorous recharge and/or association of groundwater with relatively soluble silicate minerals within the aquifer. Surface water charged with atmospheric carbon dioxide and biogenically carbon dioxide charged water infiltrating the subsurface and reacting with silicates/aluminosilicates such as plagioclase present in the geology of the district. Subsequently, Ca^{2+} and Mg^{2+} are released into the groundwater within the district. Plummer et al. (1990), Edmunds and Smedley (2000), Adams et al. (2001) have all reported from geochemical groundwater evolution studies from several parts of the world that the Ca–Mg– HCO_3 water type are commonly regarded as recharge area waters at their early phase of geochemical evolution and are rapidly circulating groundwater which have not undergone pronounced water–rock

Fig. 12 Piper trilinear (1944) diagram for groundwater within the Asutifi-North district

interaction. Some (13.6%) of the groundwater clustered towards the Na–Cl dominant section (III). It has been indicated earlier that the district is not close to the coast, and therefore, the source Na–Cl water type in groundwater within the district is not from sea aerosol spray but may be due to the influence of local rain and depicts the significance of local recharge conditions within the district. Some (11.4%) of the groundwater also clustered towards the Ca–Mg–Cl dominant section (V) where no pair dominates. The sources of the Ca–Mg–Cl water type may be due to the mixing of recharge area waters at their early phase of geochemical evolution with local rain and/ or ion-exchange between Ca–Mg–HCO₃ and Na–Cl water types. Thus, the Ca–Mg–Cl water type is characteristic of mixed waters where neither cation nor anion dominates and are reminiscent of permanent hard waters. A few (6.8%) of the groundwater also clustered towards the Ca–Mg–SO₄–Cl dominant section (I). The Ca–Mg–SO₄–Cl water type is reminiscent of permanent hard waters. 2.3% of the groundwater also clustered towards the Na–K–HCO₃ dominant section (VI) where no pair dominates. The Na–K–HCO₃ water type is characteristic of mixed waters where neither cation nor anion dominates. Shakya et al. (2019), employed the Piper (1944) trilinear plot in the investigation of deep groundwater recharge processes in an intermountain basin in the Kathmandu Valley, Nepal. The study reported that the Na–K–HCO₃, Ca–Mg–HCO₃, Na–K–HCO₃ and Ca–Mg–HCO₃ type waters were mainly found in the Kathmandu Valley. Na–K–HCO₃,

Ca–Mg–HCO₃ type waters depicted the influence of geological settings while, Na–K–HCO₃ type water was due to groundwater interaction with gneiss, and Ca–Mg–HCO₃ type water was due to the groundwater interaction limestone bedrock.

Principal component analysis (PCA)

PCA led to the extraction of three (3) main principal components which identifies the factors that influence each principal components for the physico-chemical parameters. The three principal components have accounted for approximately 73.1% of the total variance in the hydrochemical data and have eigenvalues > 1. According to Jolliffe et al. (2016), a limit of cumulative 70% variation is common to retain the PCs for any analysis. A total variance of 73.1% was therefore statistically significant to retain the PCs for this study.

Component 1 explains nearly 42.7% of the total variance (Table 4) and has strong positive loadings (> 0.75) for EC, TDS, Total hardness, Ca²⁺, Na⁺, K⁺, and a moderate positive loadings (0.75–0.50) for pH, Mg²⁺, K⁺, HCO₃[–], Cl[–] and SO₄^{2–} (Table 3) suggesting that the major ions significantly contribute to the total dissolved solids of the groundwater and can be accounted for by major geochemical processes within the aquifer. Component 2 explains approximately 21.6% of the total variance (Table 4) and has moderate positive loadings for Cl[–] and pH and weak positive loadings for SiO₂, NO₃–N, NH₄–N and HCO₃[–]. This reflects a common source, clearly silicate/aluminosilicate weathering by carbon

Fig. 13 Component plot in rotated space

dioxide charged water. The moderate to weak positive loadings for silica, HCO_3^- and pH in the groundwater suggests sorption of silica by clay minerals and signifies the influence of carbonate mineral weathering on the hydrochemistry of groundwater within the district (Yidana et al. 2012). It is most probable that dissolved silica in the groundwater within the district originates from the chemical breakdown of silicates during weathering processes. Component 2 also has a weak positive loading for $\text{NO}_3\text{-N}$ and a weak negative loading for $\text{NH}_4\text{-N}$ reflecting a common source of anthropogenic origin (possibly pollution from inorganic fertilizers such as nitrates and ammonia).

Component 3 explains approximately 8.8% of the total variance (Table 4) and has strong positive loading for $\text{PO}_4\text{-P}$. Component 3 also shows a possible pollution from inorganic fertilizers containing phosphates. The economic activity within the district includes farming where, foodstuffs such as yam, plantain, banana, vegetables, fruits and cash crops such as cocoa, oil palm and coffee are grown. Land degradation as a result of poor farming practices where indiscriminate use of nitrogen and phosphorus-based fertilizers are widespread. These are some of the human induced activities which are most likely to have anthropogenic impact on the water resources within the district.

Thus, from the PCA, it can be inferred that Component 1 delineates the main natural processes (water–soil–rock interactions) through which groundwater within the district acquires its chemical characteristics, Component 2 delineates the incongruent dissolution of silicate/aluminosilicates, as well as human-induced pollution via agriculture, while Component 3 delineates the prevalence of pollution

principally from agricultural inputs. This study is consistent with Rao et al. (2007), who employed PCA in groundwater assessment in an urban environment of Andhra Pradesh, India. The scientists reported that three (3) principal components accounted for 77.20% of the total variance with eigenvalues > 1 in the hydrochemical data. Component 1 delineated salinity processes, while Component 2 delineated alkalinity processes and Component 3 delineated the prevalence of pollution principally from agricultural inputs.

The component plot in rotated space is presented in Fig. 13. Figure 13 shows consistency with the PCA results where the major ions involved in mineralization of the groundwater have been extracted together in Component 1. SiO_2 , HCO_3^- and pH are extracted together in Component 2, and $\text{PO}_4\text{-P}$ has been extracted in Component 3.

Conclusion

The hydrogeochemical evaluation shows that the pH values of groundwater within the district are moderately acidic to neutral. Approximately 67% of groundwater acidity was due principally to the influence of aquifer materials on the chemistry of groundwater. The low pH of groundwater within the district significantly influences silicate mineral weathering which is an active process in the groundwater flow system. The study further shows that acid mine drainage processes principally produces $\text{Fe}(\text{OH})_3$ in groundwater within the district. The major ion concentrations are within the WHO (2004) Guideline values for drinking water. The relative abundance of cations and anions in groundwater within the

district was in the order of: $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$, respectively. The study further shows that plagioclase (albite and anorthite), carbonates (calcite and dolomite) dissolutions as well as ion-exchange reactions may have contributed significantly to major ion concentrations in groundwater within the district. Hydrochemical facies using Piper trilinear diagrams shows principally signatures of association of groundwater with relatively soluble silicate minerals (albite and anorthite) within the aquifer and the influence of local rain through vigorous recharge by local precipitation within the district. Other minor signatures from ion-exchange and active mixing of local flow have also been delineated. PCA has resulted in the extraction of three (3) main principal components accounting for approximately 73.1% of the total variance with eigenvalues > 1 in the hydrochemical data. The three (3) main principal components represents the main natural processes through which groundwater within the district acquires its chemical characteristics, the incongruent dissolution of silicate/aluminosilicates minerals to produce kaolinite and Na–/Ca–montmorillonite as the secondary minerals from the dissolution of plagioclase and the prevalence of pollution principally from the application of inorganic fertilizers such as nitrates and ammonia via agricultural activities within the district.

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Declarations

Conflict of interest The author declares that he has no conflict of interest.

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