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Research paper

Assessment of groundwater quality and the main controls on its hydrochemistry in some Voltaian and basement aquifers, northern Ghana

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ABSTRACT

Groundwater resources play the single most important role in the delivery of potable water to rural communities in northern Ghana, especially during the long dry season and where surface water sources are polluted or non-existent. This study sought to assess the quality and main controls on groundwater chemistry in parts of Sawla-Tuna-Kalba District in the Savannah Region of Ghana. Multivariate statistical analysis and conventional hydrochemical plots were employed in the analysis of 112 groundwater samples from the study area. Conventional graphical methods, R-mode Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA) identified dissolution of silicates and the influence of agrochemicals and domestic wastewaters as the main sources of variations in the hydrochemistry in the study area. Q-mode HCA coupled with Stiff diagrams identified Ca–HCO_3 water type in recharge areas, and Mg–Ca–HCO_3 water type, which evolves into a Ca–Na–K–HCO_3 water type in discharge areas in the groundwater flow regime. Mineral stability diagrams indicate the groundwater is stable in kaolinite, which suggests little or no restricted groundwater flow conditions. Groundwater quality for domestic purposes was assessed using the weighted arithmetic index approach. The computed water quality indices (WQIs) from the data suggest that 94% of the sampled boreholes provide groundwater of "excellent" quality for drinking purposes, whereas 5% and 1% present water of "good" and "poor" quality respectively. Spatial interpolation of the estimated WQIs suggests the quality of the groundwater in the study area is suitable for domestic purposes. The assessment of the groundwater quality for irrigation purposes suggests the water is of "excellent" to "permissible" quality and may be used for irrigation without prior treatment.

1. Introduction

Groundwater is being adopted as a preferable source of potable water supply in arid and semi-arid climates. This is due to its minimal treatment requirements, spatial availability and capacity to balance large rainfall variability as well as associated water demands during droughts and when surface water resources exceed their sustainable levels (Treidel et al., 2012; Bloomfield et al., 2019). A comprehensive groundwater assessment must reflect the several factors and processes influencing groundwater chemistry in space and time, and is prerequisite to fully understanding the groundwater system for a proper management of the resource. In this regard, researchers have adopted several strategies to assess the several sources of variation in groundwater chemistry. Most of these studies are well documented in literature (e.g. Saana et al., 2016; Hwang et al., 2017; Telahigue et al., 2018; Boateng et al., 2019; Sunkari et al., 2019). Advanced geostatistical techniques for instance have been at the forefront in this regard in recent times, especially in hydrochemical studies where they have been used to characterise groundwater flow regimes, discriminate hydrochemical facies, make predictions at unsampled locations, generate statistical models, identify sources of variations and characterise groundwater evolution (Adomako, 2011; Jing and Yufei, 2011; Kumar et al., 2011; Yidana et al., 2011, 2012a; Nur et al., 2012; Sarukkalige, 2012; Hassan, 2014; Sharma et al., 2015; Abanyie et al., 2018; Sunkari et al., 2019). In an attempt to assess the main sources of hydrochemical variation and suitability of groundwater for drinking purposes, Kumar et al. (2011) employed factor analysis, hierarchical cluster analysis (HCA) and geospatial techniques on major physicochemical parameters in the Palar river basin, India. Their study concluded that effluent discharge in the Palar river basin degraded groundwater quality in the northeast and southeast parts of the river basin and groundwater along such areas were unsuitable for drinking. HCA when combined with conventional

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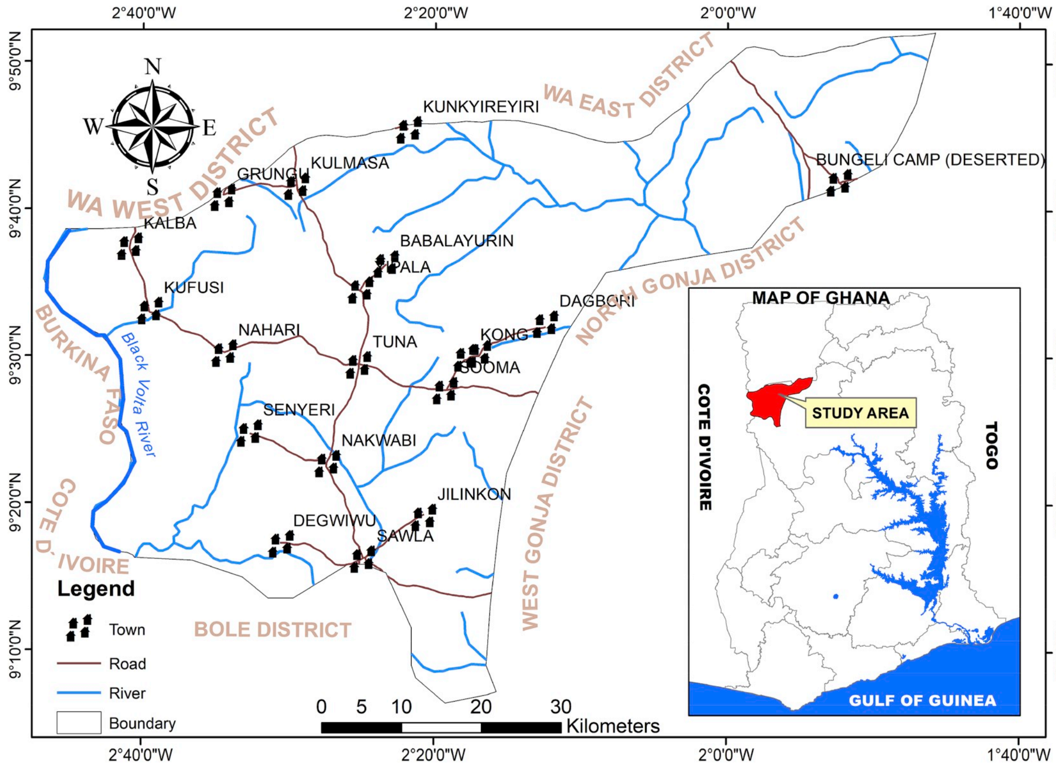

Fig. 1. Location map of the study area.

graphical techniques can help explain the evolution of groundwater and the minerals dissolved in it as it moves through the rock matrix. Belkhiri et al. (2011) demonstrated this when they employed Q-mode HCA to distinguish recharge zones from discharge areas in the groundwater flow regime in the Ain Azel plain, Algeria. Geostatistical techniques offer a wide array of powerful statistical models and tools to effectively explore and analyse hydrochemical data. However, employing these techniques requires an in-depth understanding of the prevailing environmental conditions in the study area such as geology, hydrogeology, topography, weather conditions and dominant anthropogenic activities.

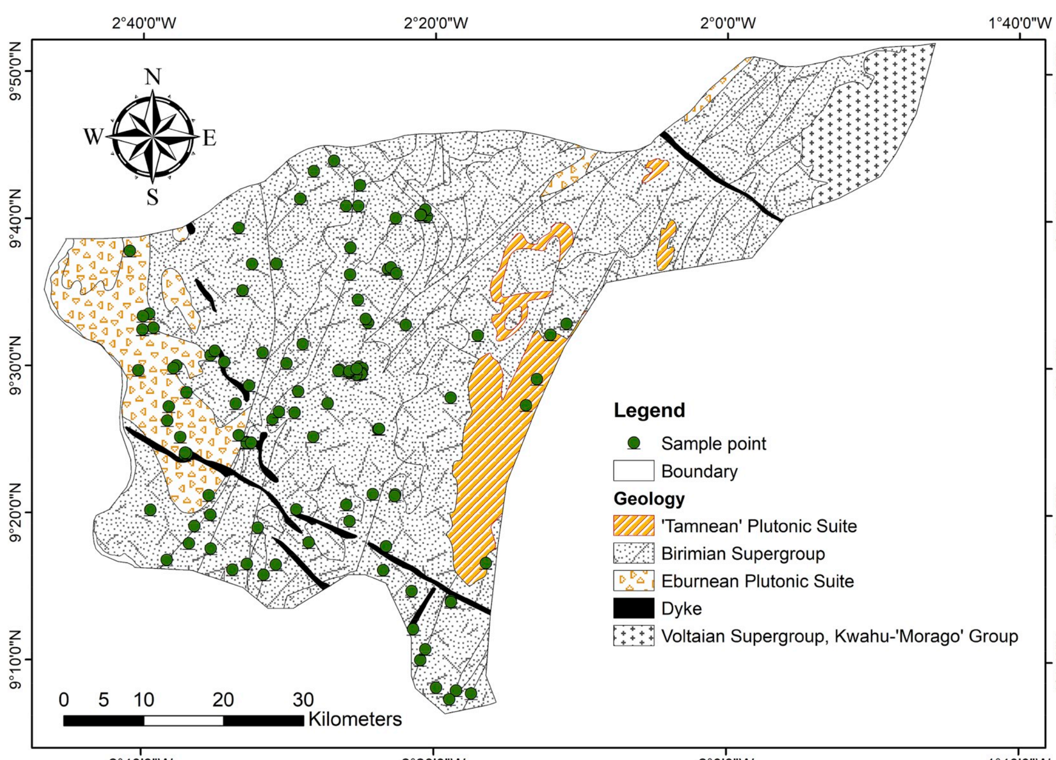

Fig. 2. Geological map of the study area showing sampled points.

Geostatistical techniques have been employed extensively in groundwater studies in Ghana. For instance, with the aim of unveiling the key factors influencing fluoride concentrations in some parts of Northern Region Ghana, Yidana et al. (2012a) utilised principal component analysis (PCA) coupled with cluster analysis to explain the hydrochemistry and factors influencing fluoride enrichment and other ions of the groundwater in the middle Voltaian aquifers. They also adequately distinguished the various facies in the groundwater flow regime using Q-mode HCA. Furthermore, Sunkari et al. (2019) combined multivariate statistics and mass balance techniques to assess the drivers of groundwater chemistry in Ga West, Ghana. Their study revealed silicate and carbonate weathering, seawater intrusion and anthropogenic activities as the main controls on groundwater chemistry in the district. Other similar studies in Ghana are well documented in Helstrup et al. (2007); Banoeng-Yakubo et al. (2009); Yidana et al. (2010); Loh et al. (2016); Abanyie et al. (2018).

It follows therefore, that when applied properly, with adequate knowledge of the terrain, geostatistical techniques can be used to satisfactorily characterise groundwater systems. This study adopts similar methodology in addition to conventional and mass balance hydrochemical models to unveil the relationships among water parameters and the main influence on groundwater chemistry from the basement aquifers in the Sawla-Tuna-Kalba District in northern Ghana as well as assesses its suitability for domestic and irrigation purposes.

2. Study area

The study area (Fig. 1) is located in the western part of the Savannah Region of Ghana. It lies between latitudes 8°40′ and 9°40′ north and longitudes 1°50′ and 2°45′ west. The study area shares common boundaries with Wa West and Wa East Districts to the North, Bole District to the South, West Gonja and North Gonja Districts to the East, and La Cote d'Ivoire and Burkina Faso to the West. It has a total land area of about 4226.9 km^2 and a population of 99,863 (Ghana Statistical Service, 2010).

Generally, the topography of the study area is undulating, with elevation ranging between 245 m and 350 m. The Black Volta River runs through the study area along the western border and drains the area through several tributaries and streams. The area lies within the Tropical continental climate, and generally is one of the driest parts of the country. It experiences a single rainfall season that occurs between early May and late October, with the highest rainfall experienced between August and September (Dickson and Benneh, 1995). Relative humidity is high during the rainy season (65–85%) but may fall to as low as 20% during the dry season. Monthly mean rainfall ranges between 200 mm and 300 mm, with an annual average of about 1100 mm (Sawla-Tuna--Kalba District Assembly, 2014).

2.1. Geology and hydrogeology

The study area is principally underlain by about 80% Birimian rocks with the other 20% being granitoids and Kwahu-Morago Group of the Voltaian Supergroup (Fig. 2). The Birimian consists of metamorphosed volcanic and sedimentary rocks, which form five subparallel belts of volcanic rock separated by broad "basins" of sedimentary rocks (Kesse, 1985). Rocks of the Birimian Supergroup have been divided into metasedimentary and metavolcanic rocks (Junner, 1935, 1940; Bates, 1955). The Birimian metasedimentary are made up of greywackes with turbidite features, phyllites, slates, schists, weakly metamorphosed tuffs and sandstones whiles the Birimian metavolcanics comprise rock types such as lava flows and dyke rocks of basaltic and andesitic composition. Most of these rocks have now been metamorphosed to hornblende actinolite-schists, calcareous chlorite schists and amphibolites (Kesse, 1985). The Birimian Supergroup is intruded by granitoids of the Eburnean and 'Tamnean' Plutonic Suites. In Ghana, four main types of granitoids are recognized to be associated with the Birimian Supergroup. These include; the Winneba, Bongo, Dixcove and the Cape Coast type granites. The Cape Coast and Dixcove granites are seen to be present in the current study area. The Cape Coast type granitoids occur only within the Birimian metasediments. This group also includes gneisses, which are especially well developed in the metasediments (Banoeng-Yakubu et al., 2011). Dixcove-type granitoids are metaluminous and typically dioritic to granodioritic in composition, and intrude the Birimian metavolcanic rocks. They are typically hornblende bearing and are commonly associated with gold mineralisation where they occur as small plutons within the volcanic belts (Kesse, 1985). The granitoids are massive in outcrop, do not have a compositional banding or foliation, and are thus generally considered post-deformation (Banoeng-Yakubu et al., 2011). The Kwahu-Morago Group of the Voltaian Supergroup consist mainly of sandstone, which are white, medium-grained, cross-bedded, flaggy, and quartzose.

Hydrogeologically, the study area falls within three main hydrogeological provinces, namely Birimian Province, Voltaian Province, and Crystalline Basement Granitoid Complex Province (Dapaah-Siakwan and Gyau Boakye, 2000). Groundwater in the Birimian Province occurs mainly in the saprolite, saprock and in the fractured bedrock. The most productive zones in terms of groundwater delivery in the Birimian Province comprise the lower part of the saprolite and the upper part of the saprock, which usually complement each other in terms of permeability and storage (Carrier et al., 2008). The upper, less permeable part of the saprolite can act as a semi-confining layer for this productive zone, while the lower, usually saturated part of the saprolite is characterised by lower secondary clay content, thus creating a zone of enhanced hydraulic conductivity (Banoeng-Yakubu et al., 2011). Generally, areas underlain by the Birimian rocks display deeper weathering than areas underlain by the granitoids.

Banoeng-Yakubo (1989) identified three types of basement aquifers. These are the weathered rock aquifers, which are fracture related, the fractured quartz-vein aquifers and the fractured unweathered aquifers. Banoeng-Yakubu et al. (2011) underscored that in the Birimian Province aquifers, the saprolitic zone is a combination of the topsoil, the underlying lateritic soil, the highly weathered zone and the moderately weathered zone. Successful boreholes drilled through the rocks of the Birimian and the Tarkwaian range between 35 and 55 m with an average of 42 m (Agyekum, 2004). Carrier et al. (2008) also recorded borehole depth in a similar range of 35 and 55 m with an average of 50 m in the granitoids. Data collated from WRI-CSIR shows that the depth to water table falls within 4–37 m with an average of 21 m. There is no well-defined local groundwater flow regime, however, the groundwater flow within the study area follows the regional flow regime, which is from north to south and to a large extent toward the south-western parts of the study area. The aquifer transmissivity of the productive zones of the Birimian Province has been reported by Banoeng-Yakubu et al. (2011) to range between 0.2 m^2/d and 119 m^2/d, with an average of 7.4 m^2/d. The Kwahu-morago Group, which is composed of 'Yabraso' sandstone formation, has been identified as good aquifer zone based on available data from drilling projects within the area. The basement rocks are characterised by little or no primary porosity, and therefore the hydrogeology of the area is controlled by secondary permeabilities resulting from weathering and fracturing of the rock which has enhanced the storage and transmissive properties of the rocks to form groundwater reservoirs (Darko et al., 2006; Yidana et al., 2012b).

3. Methodology

Data of groundwater samples collected from boreholes in the study area were obtained from Hydronomics Ghana limited in Accra. Standard protocols for water sampling and storage as prescribed in APHA (2005); USGS (2006) and Canada CCME (2011) were adopted. One hundred and twelve (112) samples collected 500 ml in pre-cleaned sterilized poly propylene plastic bottles were stored in cool boxes (about 3 °C) and transported to the Water Research Institute of the Council for Scientific and Industrial Research (WRI-CSIR) laboratory for major and trace cations and anions analyses whiles pH, electrical conductivity (EC) and Temperature were determined on the field with the aid of a multi-parameter portable meter (PELI 1521) from HANNA Instruments. In the laboratory, the samples were stored at 4 °C in a refrigerator for about a week before they were analysed. Different methods (i.e. gravimetric (TDS), titrimetric (Ca, Total hardness, alkalinity), SPADNS (F^-), turbidimetric (SO_4^{2-}), argentometric (Cl^-), atomic absorption spectrometry (As, Mn, Fe, HCO_3^-), flame photometry (K, Na^+, Mg^{2+}), hydrazine reduction (NO_3^-), Stannous chloride (PO_4^{2-})) were used to analyse the major, minor and trace elements. The dataset was subjected to an internal consistency test using the charge balance error (CBE) to test its accuracy (equation (1)). A charge balance error value within ±5% is generally acceptable and shows that the laboratory analysis of the parameters are a good balance of the cations and anions (Appelo and Postma, 2005). In view of this, samples that recoded CBE values above ±5% were dropped from the analysis.

$$\text{C.B.E} = \frac{\sum mc|zc| - \sum ma|za|}{\sum mc|zc| + \sum ma|za|} \times 100 \quad (1)$$

Where m_c and m_a, and z_c and z_a are respectively molar concentrations of major cations and anions, and charges of cations and anions.

Similarly, the resulting datasets were subjected to normality test, since optimal multivariate statistical analyses assume Gaussian distribution of datasets. Datasets that were not normally distributed were log-transformed and/or standardised to their z score (equation (2)) values.

$$z = \frac{x - \mu}{s} \quad (2)$$

Where x, μ and s are respectively the measured value, mean and standard deviation of the parameter.

The transformed datasets were subjected to R-mode and Q-mode hierarchical cluster analysis (HCA). The Q-mode HCA is used to discriminate the spatial associations or evolution of the groundwater into various types in space and/or time, whereas R-mode is used to determine and rank the sources of variation in the hydrochemistry. Although several similarity/dissimilarity and agglomerative techniques are available in HCA, the squared Euclidean distance and Ward's agglomeration method were employed in this study, since a combination of these two have been identified to yield the best outcomes in HCA (Davis, 1986; Yidana et al., 2010, 2012a). For significant and optimal stochastic analysis, parameters with large missing datasets such as F, Fe, Mn and As in most cases were excluded from the cluster analysis.

Principal component analysis (PCA) was also applied to the dataset to identify the main controls on groundwater chemistry. PCA is a data dimension reduction technique that reveals the significant components/factors to aid interpretation of a large set of data and to visualise the correlations between the variables and hopefully be able to limit the number of variables. PCA was performed using the correlation matrix, which brings the measurements onto a common scale and the principal components sorted in a diminishing order of variance, such that the most important principal components are listed first. To ensure that the extracted components did not correlate with each other, an orthogonal (varimax) rotation technique was used.

Assertions made in relation to the hydrochemical associations and processes based on the multivariate statistical techniques were supported by employing conventional hydrochemical plots and mineral stability diagrams to further establish the main controls on groundwater chemistry and to identify the most stable mineral phases in the groundwater flow system.

The quality of the groundwater was also assessed for drinking and irrigation purposes. Quality assessment for domestic purposes was based on a modified form of the water quality index (WQI) approach (Sahu and Sikdar, 2008), which is a weighted arithmetic index method. The resultant water quality indices estimated from this method were spatially interpolated using inverse distance weighting (IDW) technique. In order to minimise the errors associated with the spatial prediction, the interpolation was limited to places in the study area with optimal sample-point distribution, such that places with little/no sample points were excluded from the interpolation. Irrigation quality of the groundwater on the other hand was assessed using the Wilcox (1955) and United States Salinity Laboratory (USSL, 1954) diagrams.

Table 1
Statistical summary of the concentrations of the physicochemical parameters.

Parameter	Mean ($\bar{X}$)	Std. Dev (s)	Minimum	Maximum
pH	6.86	0.61	5.87	9.99
EC	429	196	101	1040
TH	158.0	47.7	50.0	270.0
Alkalinity	178.3	57.5	70.0	366.0
Ca^{2+}	33.6	14.4	9.6	77.8
Mg^{2+}	18.0	6.4	3.4	32.5
Na^+	31.0	17.7	7.5	97.8
K^+	4.9	1.7	1.4	11.0
HCO_3^-	217.5	70.2	85.4	447.0
SO_4^{2-}	12.8	14.5	2.5	65.2
Cl^-	18.8	13.1	3.0	70.5
NO_3^-	0.40	0.75	<0.01	5.3
PO_4^{2-}	0.08	0.09	<0.01	0.39
F^-	0.8	0.4	0.2	2.4
Fe	0.16	0.47	<0.01	4.13
Mn	0.06	0.07	<0.01	0.29
SiO_2	59.1	11.6	28.0	87.6
As	<0.01	0.01	<0.01	0.08

4. Results and discussions

The statistical summaries of the analysed parameters are presented in Table 1. Most of the major chemical parameters display high ranges of variance, suggesting variable sources and factors influence and contribute to the concentration of these parameters of the groundwater in the study area. Generally, concentrations of the major chemical parameters are within the acceptable WHO recommended ranges for potable water (WHO, 2017).

However, there are a few cases where some hydrochemical parameters, which mostly occur as outliers, fall outside the acceptable WHO (2017) ranges for potable water. One instance is the occurrence of high fluoride levels recorded in some parts of Gindabo and Tuna in the central sections of the study area, which may be associated with the leaching and weathering of fluorite and/or the influence of alkaline water types in the area. Alkaline waters have been reported to retard the adsorption of fluoride onto the surfaces of clay minerals (Viero et al., 2009). pH presents the least variance among the major chemical parameters and has ranges falling outside (5.87–9.99) the WHO (2017) recommended range of 6.5–8.5, signifying a slightly acidic to slightly alkaline groundwater system.

4.1. Assessment of the main sources of variation in groundwater chemistry

Results of Pearson correlation (r) analysis are presented in Table 2. Correlation analysis provides a quick way to visualise the relations between two parameters for purposes of drawing inferences. It is obvious from the results that the main contributors to EC in the study area are Ca^{2+}, Na^+, HCO_3^-, SO_4^{2-}, Cl^- and F^- since these parameters have significant correlations (≥0.50) with EC. Similarly, bicarbonate shows significant relation with Na^+ and Ca^{2+}, which is consistent with silicate weathering (Freeze and Cherry, 1979), and possibly influenced by precipitation.

R-mode hierarchical cluster analysis (HCA) and principal component analysis (PCA) have been used to further unearth the main chemical processes controlling groundwater chemistry in the study area. The

Table 2
Pearson correlation analysis of hydrochemical parameters.

	pH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	PO_4^{2-}	F^-	Fe	Mn	SiO_2	As	EC
pH	1.00															
Ca^{2+}	0.30	1.00														
Mg^{2+}	0.11	0.14	1.00													
Na^{+}	0.32	0.51	0.04	1.00												
K^{+}	−0.02	0.35	0.18	0.14	1.00											
HCO_3^-	0.42	0.67	0.47	0.69	0.29	1.00										
SO_4^{2-}	0.06	0.50	0.00	0.54	0.20	0.15	1.00									
Cl^-	0.07	0.47	0.13	0.39	0.14	0.09	0.61	1.00								
NO_3^-	−0.08	0.24	0.13	0.21	0.19	0.08	0.35	0.42	1.00							
PO_4^{2-}	−0.02	−0.15	−0.23	−0.28	−0.11	−0.31	−0.13	−0.04	−0.17	1.00						
F^-	0.42	0.38	0.01	0.69	0.24	0.53	0.36	0.23	0.02	−0.25	1.00					
Fe	0.13	0.24	0.00	0.31	0.19	0.17	0.40	0.27	0.15	0.07	0.47	1.00				
Mn	0.17	0.28	0.36	0.22	0.30	0.28	0.24	0.31	0.36	−0.24	0.25	0.32	1.00			
SiO_2	−0.27	−0.40	0.00	−0.45	−0.10	−0.42	−0.26	−0.16	−0.04	0.12	−0.44	−0.14	0.00	1.00		
As	0.04	0.00	0.16	0.01	0.06	0.10	−0.05	−0.04	0.03	−0.07	0.03	−0.02	0.01	0.00	1.00	
EC	0.34	0.78	0.37	0.76	0.34	0.76	0.58	0.55	0.36	−0.35	0.60	0.39	0.39	−0.43	0.06	1.00

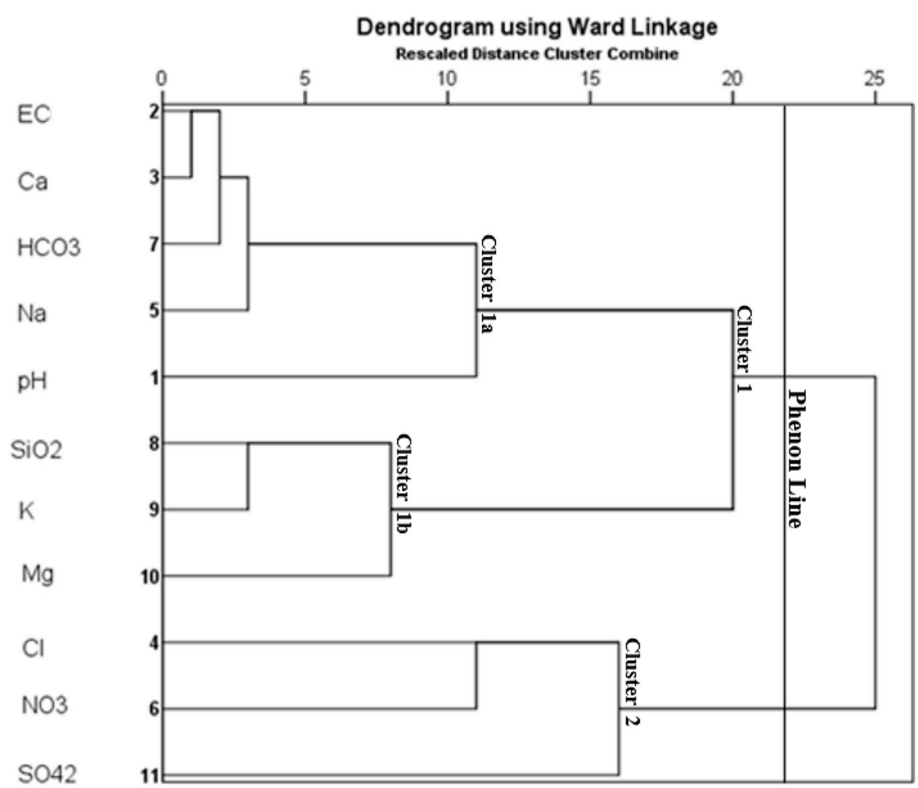

Fig. 3. Dendrogram from R-mode cluster analysis.

dendrogram (Fig. 3) for the R-mode cluster analysis presents the visual associations among the parameters with a phenon line drawn at a linkage distance of about 22. Although the definition of clusters based on the distance of the phenon line is subjective, it is informed by the researcher's understanding of the combining environmental factors such as the geology, hydrogeology and human activities which prevail in the study area and are likely to affect the chemistry of groundwater (Yidana et al., 2012a). The phenon line is drawn such that too many or too few clusters are not generated since the interpretation might be difficult, defeating the purpose of cluster analysis, or some important hydrochemical processes might be omitted.

Notwithstanding the semi-objectivity, two clusters were generated which represent two main groundwater associations and/or processes. Cluster 1 consists of Na^+, Ca^{2+}, EC, HCO_3^-, pH, K, Mg and SiO_2 which represents the dominance of rock-water interaction; dominated by dissolution of silicate minerals in the rocks of the area. The close association of EC, Ca^{2+}, HCO_3^-, Na^+ and pH in cluster 1a suggests the dissolution of feldspars in the sandstones found in the study area. The reaction of carbon dioxide in the atmosphere and precipitation and possibly within the soil zone results in the formation of carbonic acid, which dissolves such minerals during infiltration, thereby releasing HCO_3^- and the associated ions. Cluster 1b on the other hand consists of SiO_2, K^+ and Mg^{2+}, at a much shorter linkage distance than cluster 1a, and therefore presents the most similar members of the same cluster given the shorter linkage distance (Yidana et al., 2011), relative to cluster 1a and cluster 2. Cluster 1b probably represents silicate mineral weathering, especially micas such as biotite which are also present in the study area (Sawla Tuna Kalba District Assembly, 2014).

The second cluster links NO_3^-, SO_4^{2-} and Cl^-. Cluster 2 represents the influence of agrochemicals and domestic wastewaters, which are common pollutants of groundwater in agrarian settlements such as the study area (Han et al., 2016).

Table 3a
Final factor loadings for the water quality parameters.

	Component	
	1	2
HCO_3^-	.923	-.050
EC	.805	.491
Na^+	.782	.328
Ca^{2+}	.738	.397
SiO_2	-.663	-.011
Cl^-	.175	.843
SO_4^{2-}	.305	.770
NO_3^-	-.009	.728

Table 3b
Communalities of parameters on factor model.

	Initial	Extraction
EC	1.000	.889
Ca^{2+}	1.000	.702
HCO_3^-	1.000	.854
Na^+	1.000	.720
SO_4^{2-}	1.000	.686
Cl^-	1.000	.741
NO_3^-	1.000	.531
SiO_2	1.000	.520

Results of principal component analysis (PCA) revealed two main components just like the R-mode cluster analysis, and these accounted for about 70% of the total variance in the hydrochemistry (Table 3). The factors were extracted based on variables with communalities of 0.5 and above (Kaiser, 1960), and variables below the set lower limit such as K^+, PO_4^{2-}, As, Mn and Fe were excluded from the analysis. Communalities measure the proportion of each variable's variance that can be explained by the factors. Therefore, variables which loaded highly with more than one component such as Mg^{2+} and pH were dropped, since these variables had duplicate effects and could not be used to explain a particular unique process in the hydrochemistry.

The first component which accounts for over 40% of the total variance in groundwater chemistry in the study area has high positive loadings for HCO_3^-, EC, Na^+, Ca^{2+} and high negative loading for SiO_2. It can be deduced from the correlation analysis, HCA and PCA that Component 1 represents the dissolution of silicates, particularly, the feldspars in the sandstones underlying the area, thus confirming the findings from cluster 1a (Fig. 3). The negative loading of SiO_2 with component 1 also suggests that the silica in the groundwater does not contribute significantly to the electrical conductivity, which is in line with the results of the correlation analyses (Table 2). A plot of Na versus Cl (Fig. 4) suggests that the dissolution of halite is not the main source of Na^+ in the groundwater and thus the dissolution of silicate minerals could be the source of this ion in the groundwater. The strong correlation between F^- and Na^+ ($r = 0.69$) as shown in Table 2, possibly suggests the dissolution of minerals such as villiaumite and fluorapatite, which are common constituents of the bedrock of the study area (Yidana et al., 2012a).

Table 3c
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	4.136	51.697	51.697	4.136	51.697	51.697	3.218	40.231	40.231
2	1.426	17.829	69.526	1.426	17.829	69.526	2.344	29.294	69.526
3	.737	9.208	78.733						
4	.642	8.028	86.761						
5	.504	6.297	93.058						
6	.363	4.533	97.592						
7	.129	1.608	99.200						
8	.064	.800	100.000						

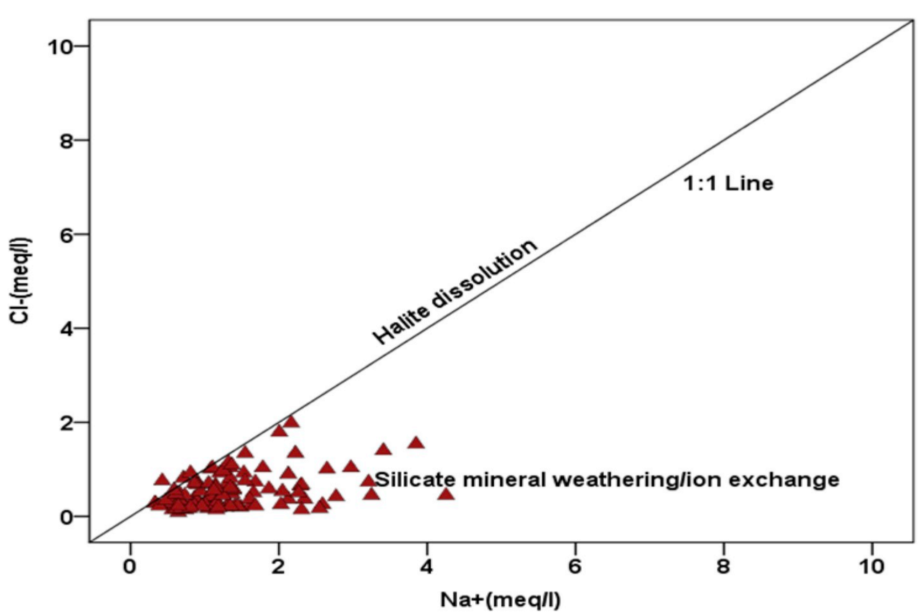

Fig. 4. Molar concentrations of Na^+ versus Cl^- suggesting silicate weathering/ion exchange in the hydrochemistry of the study area.

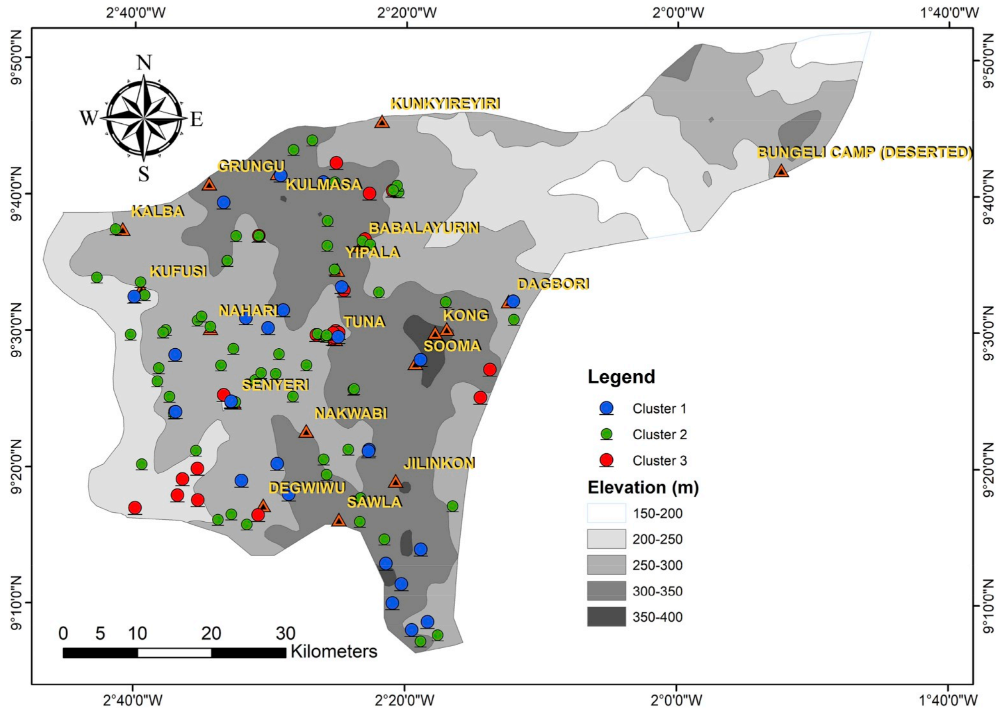

Fig. 5. Spatial distribution of the cluster from Q-mode HCA.

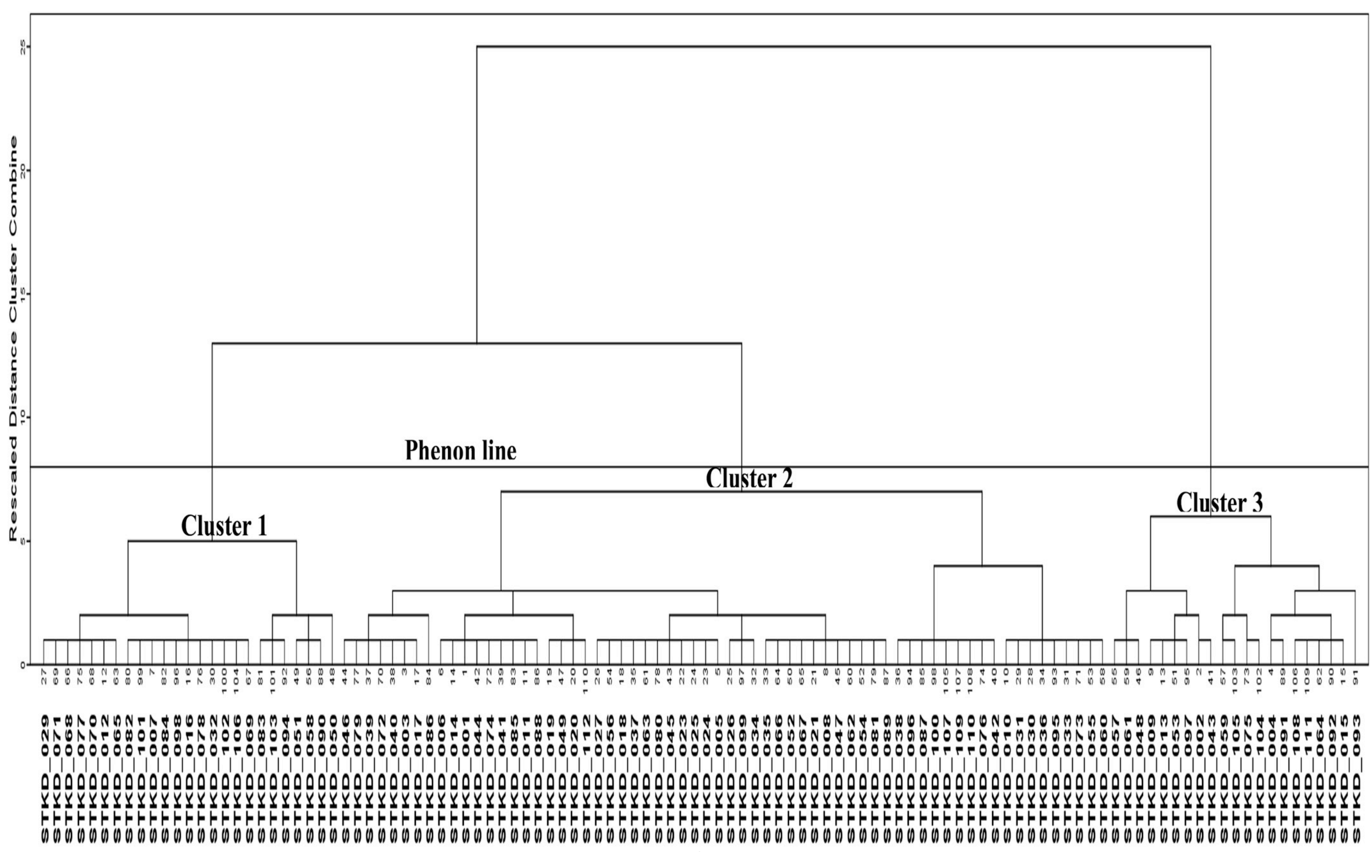

Fig. 6. Dendrogram from the Q-mode HCA showing the spatial groundwater associations.

Component 2 on the other hand loads highly with Cl^-, SO_4^{2-} and NO_3^- and represents the influence of agrochemicals and domestic wastewaters, as these ions are common constituents of such pollutants. Since the study area is composed mainly of agrarian communities, with farming practices, which involves the use of organic and inorganic fertilizers such as manure and NPK, groundwater is likely to be polluted by such

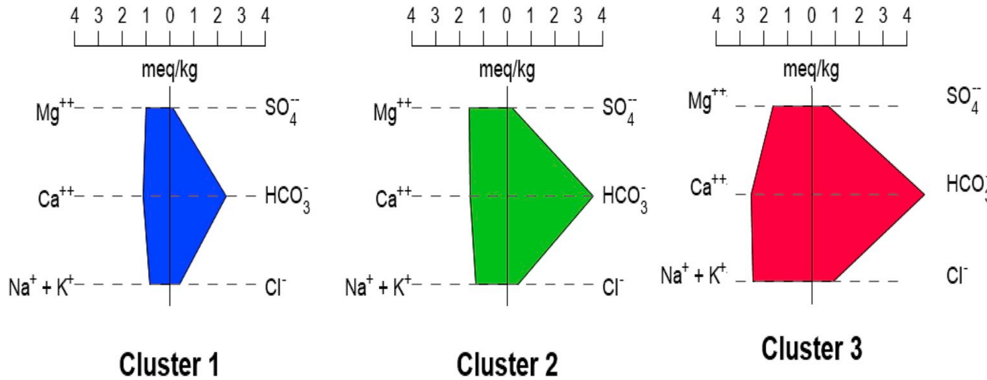

Fig. 7. Stiff diagrams made from average concentrations of major ions from the three clusters from Q-mode HCA.

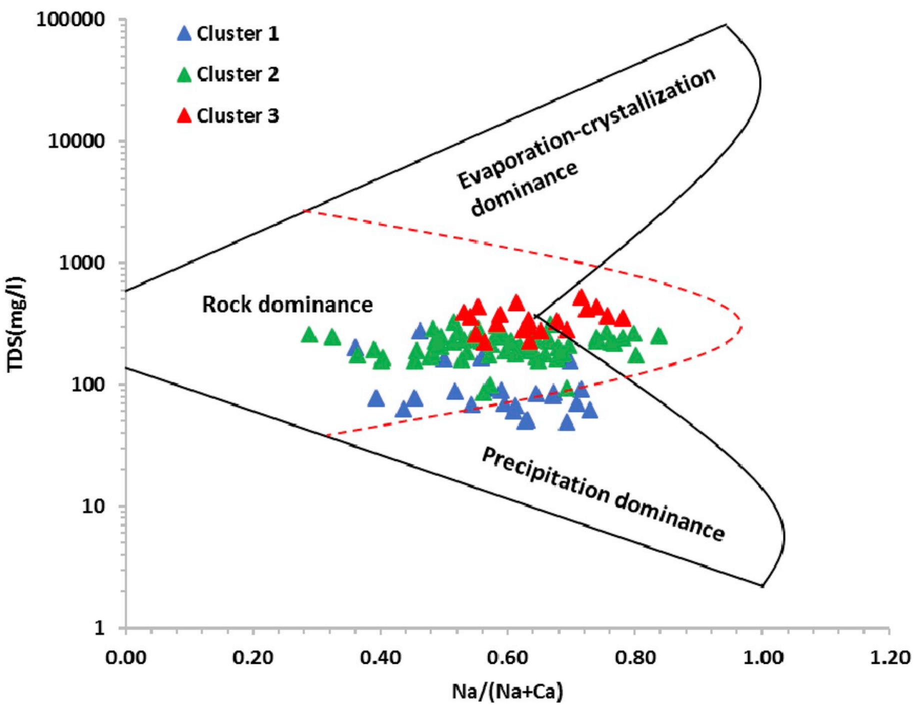

Fig. 8. Gibbs diagram showing the main sources of variation in groundwater chemistry for the study area.

chemicals in the study area (Cobbina et al., 2012).

Q-mode HCA resulted in a dendrogram (Fig. 6) showing three main spatial associations in the hydrochemistry in the study area. Average concentrations from the three clusters are presented with Stiff diagrams (Fig. 7). Generally, aquifers of the Birimian deliver groundwater of low ionic concentrations since their hydrochemistry is mainly influenced by silicate mineral weathering (Yidana et al., 2012a). Notwithstanding, the three clusters exhibit varying degrees of ionic concentrations and suggest a flow pattern in the groundwater system. It is obvious from Fig. 7 that on the average cluster 1 presents the least mineralised groundwater system. Cluster 1 is mainly composed of samples from around Kong, Sooma, Jilinkon, Nahari and Grungu, which are generally high elevation locations in the study area (Fig. 5). Conversely, cluster 3 presents the highest mean concentration of the major ions and TDS, and is found at locations with low elevations such as Babalayurin, Degwiwu, Kalba, and generally the south western portions of the study area, whereas cluster 2 occurs between clusters 1 and 3 (Fig. 5).

In recharge areas, the concentration of ions in groundwater is usually low and similar to the precipitation in the area, but as the water travels through the subsurface and dissolves minerals and other materials, its ionic content increases with time. This explains why clusters 1 and 3 have been designated as recharge and discharge zones respectively, consistent with topographically-driven groundwater flow (Fitts, 2002), whereas cluster 2 samples are considered to represent a transition between clusters 1 and 3. This is clearly demonstrated by the Stiff diagrams in Fig. 7.

It is apparent from the Stiff diagrams (Fig. 7) that cluster 1 is a Ca–Mg–HCO_3 water type, whereas cluster 2 is Mg–Ca–HCO_3 water type which evolves into a Ca–Na–K–HCO_3 water type in cluster 3. The dissolution of villiaumite and fluorapatite is plausible when the water had enough time to interact with the rocks as it evolves towards discharge areas thus increasing the concentration of Na in those areas. Similar water types were identified by Cobbina et al. (2012) in the Voltaian and Basement aquifers in the Savannah Region. This is in tandem with the assertions made above from Table 3 and Fig. 4, that dissolution of silicates plays a significant role, explaining over 40% of the total variance in groundwater chemistry in the study area.

A Gibbs (1970) diagram plotted for all three clusters clearly indicates rock dominance as the main source of the dissolved ions in groundwater from the study area (Fig. 8). However, the hydrochemistry of cluster 1 samples is largely influenced by the chemistry of precipitation in the area, which is characteristically low in dissolved ions and high in

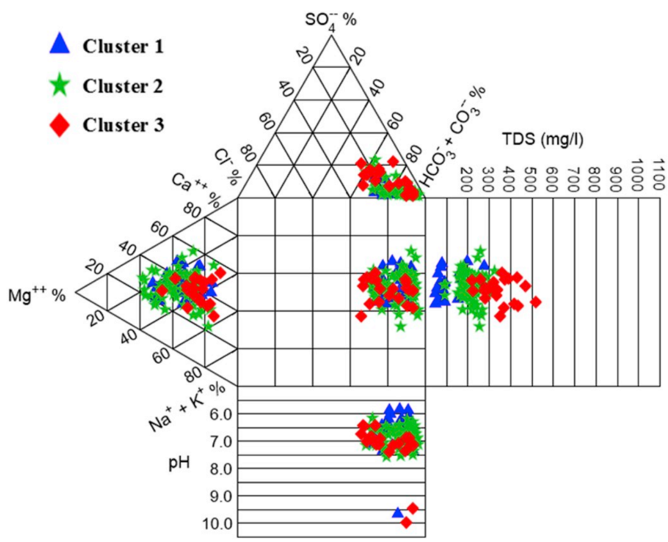

Fig. 9. Durov diagram showing the predominant groundwater types in the study area.

bicarbonate as a result of the CO_2-charged rainfall. Although samples from clusters 2 and 3 plot within the rock dominance section, it can be seen that samples from cluster 3 plot much closer to rock dominance–evaporation-crystallization line than the rock dominance–precipitation line. This supports the argument that waters from cluster 3 are more enriched in dissolved ions as a result of the longer interaction of the groundwater with the rock matrix.

Generally, groundwater from the study area is clearly a mixed cation fresh water type dominated by bicarbonate (HCO_3>SO_4+Cl), as demonstrated by the Stiff diagrams (Fig. 7). Durov (1948) diagram has been used to discriminate the hydrochemistry further. From Fig. 9, it is apparent that most of the groundwater samples (42%) are dominated by Ca–HCO_3, implying the dominance of alkaline earths over alkali (thus Ca + Mg > Na + K), whereas 36% and 20% are respectively Mg–HCO_3 and Na + K–HCO_3 fresh water types. Cluster 3 samples plot closer to the Na + K field and further away from the Ca and Mg fields, with corresponding high TDS and pH values (Fig. 9), confirming that these waters have had longer time to interact with the rock matrix and the surrounding environment. The low pH values mainly contributed from precipitation, as seen in cluster 1 samples, are neutralized as the water interacts and dissolves the rock material as it transits the recharge zones and evolves into a more ionically enriched water in cluster 3.

The mineral stability diagrams for $NaO–Al_2O_3–SiO_2–H_2O$ and $Al_2O_3–SiO_2–H_2O$ are presented in Fig. 10. Both plots indicate that the most stable silicate phase in the aquifers is kaolinite, indicating the incongruent weathering of silicate minerals such as biotite and muscovite, and suggests that the groundwater in the aquifer is relatively young to intermediate in its flow regime and age. This implies that there is little or no restricted groundwater flow such that the residence time is not long enough to allow for significant silica leaching into the groundwater (Edet and Okereke, 2005; Yidana et al., 2008a,b; Loh et al., 2016).

4.2. Groundwater quality evaluation for domestic use

The quality of the groundwater has further been examined for its potability, using the water quality index (WQI) approach, modified after Brown et al. (1972). This approach is a weighted arithmetic approach, which involves a series of steps to arrive at a single value (index), which describes the overall quality of water in space and time. The suitability of groundwater in this study was based on the standards set by the World Health Organisation (WHO, 2017) for domestic drinking water. In the first step, water quality parameters of concern are assigned weights (*wi*) based on their importance and health implications when present in drinking water. F^-, NO_3^- and As were assigned a maximum of 5 based on their relative importance in drinking water. The rest of the parameters (pH, TDS, TH, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}, PO_4^{3-}, Fe and Mn) were assigned weights of 1–5 also based on their relative importance and health implications when present in drinking water. Secondly, the

Table 4
Standards, weights and relative weights used for WQI computation.

Chemical Parameter	Objective to be met (Si) (mg/l)	Weight (wi)	Relative weight (Wi)
pH	7.5	4	0.0943
TDS	500	4	0.0755
TH	200	4	0.0755
Ca^{2+}	200	2	0.0377
Mg^{2+}	150	2	0.0377
Na^+	200	2	0.0377
K^+	30	2	0.0377
Cl^-	250	3	0.0566
SO_4^{2-}	250	3	0.0566
NO_3^-	50	5	0.0943
PO_4^{3-}	0.7	4	0.0755
F^-	1.5	5	0.0943
Fe	0.3	3	0.0566
Mn	0.4	4	0.0755
As	0.01	5	0.0943

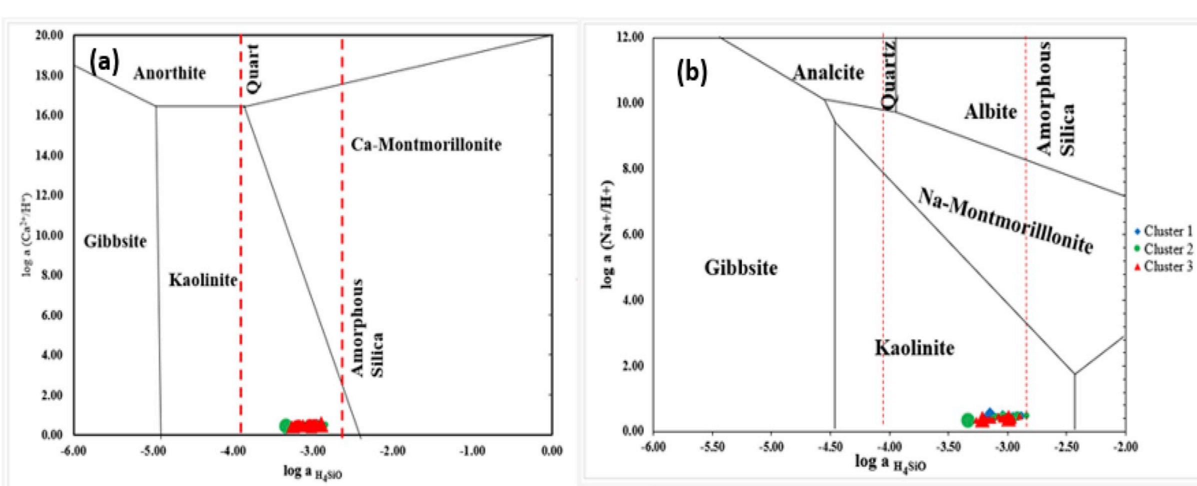

Fig. 10. Mineral stability diagrams for the (a) $Ca–Al–SiO_2–H_2O$ system, (b) $Na–Al–SiO_2–H_2O$ system at 1 atm and 25 °C.

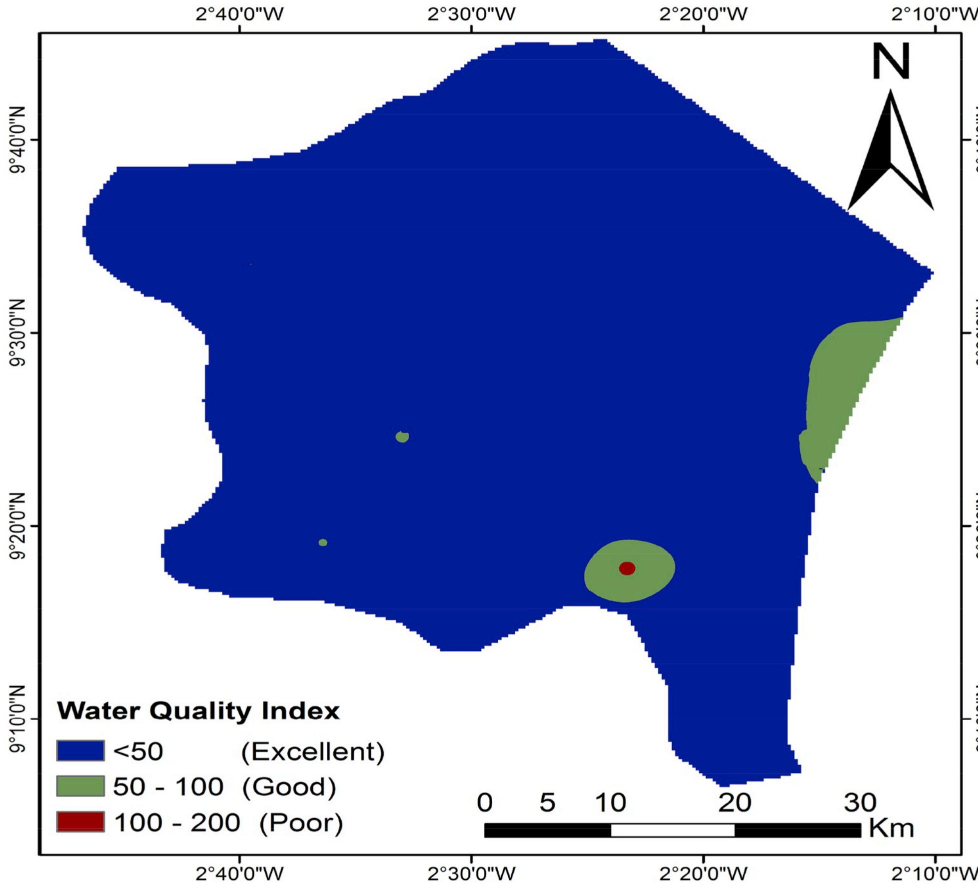

Fig. 11. Spatial distribution of water quality indices reclassified after Sahu and Sikdar (2008).

relative weight (Wi) of each parameter was computed as a fraction of the total weights computed from the fifteen parameters (Table 4) based on equation (3).

$$\mathrm{Wi}\frac{\mathrm{wi}}{\sum \mathrm{wi}} \tag{3}$$

Lastly, a quality rating scale (qi) was calculated for each parameter by dividing its concentration by the set objective (WHO standard) and multiplying by 100 (equation (4)).

$$\mathrm{qi} = \frac{\mathrm{Ci}}{\mathrm{Si}} \times 100 \tag{4}$$

Where Ci and Si are respectively parameter concentration and set objective.

The sub-index and WQI are determined respectively using equations (5) and (6).

$$\mathrm{Si} = \mathrm{Wi} \times \mathrm{qi} \tag{5}$$

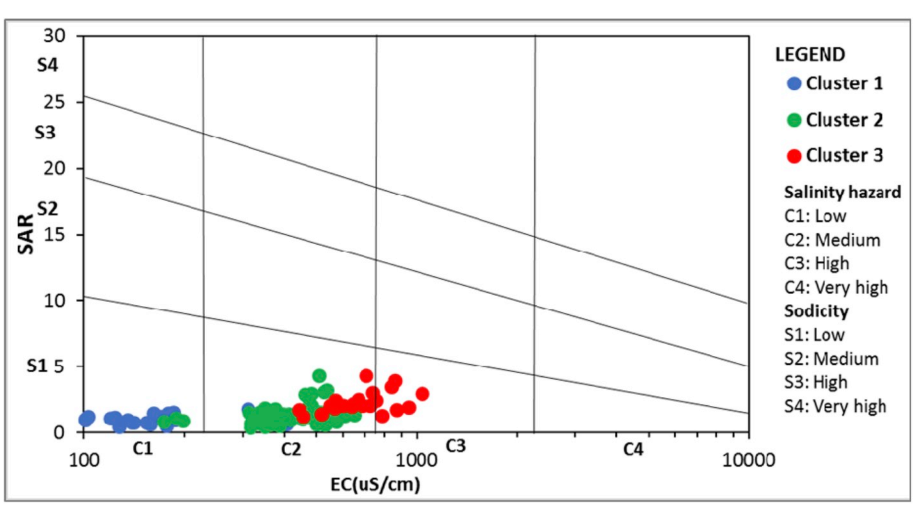

Fig. 12. Groundwater quality classification for irrigation in the study area (USSL, 1954).

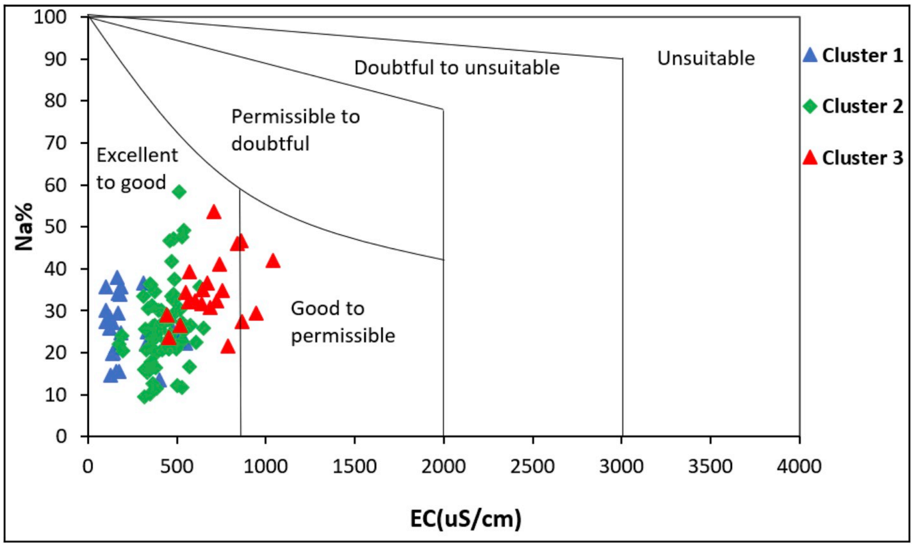

Fig. 13. Groundwater quality assessment for the study area based on Wilcox (1955) diagram.

$$\mathrm{WQI} = \sum_{n=1}^{n} \mathrm{Si} \quad (6)$$

The calculated WQIs are categorised according to Sahu and Sikdar (2008) as "excellent water" (WQI <50); "good water" (WQI = 50–100); "poor water" (WQI = 100–200); "very poor water" (WQI = 200–300); and "unsuitable for drinking" (WQI >300).

The computed WQIs have been spatially interpolated based on an inverse distance weighting (IDW) technique, which proved to be the most appropriate interpolation technique as a result of the smallest root mean square error associated with it (RMSE = 0.852). The output was reclassified according to Sahu and Sikdar (2008) (Fig. 11). The estimated WQIs ranged from 16.64 to 132.15, with about 94% of the water classified as being "excellent" for drinking purposes, whereas 5% and 1% are considered "good" and "poor" quality respectively (Fig. 11). The poor water arises from two samples, STKD_086 and STKD_93 located at Sawla and Soomia, which are characterised by elevated levels of fluoride, arsenic and Fe. These samples generally have high TDS values, and the contamination could be attributed to localised leaching of such ions into the groundwater system.

4.3. Assessment of groundwater quality for irrigation purposes

The presence of sodium ion in groundwater is of grave concern due to its ability to affect the permeability of soil as well as offset the osmotic pressure of plants. An offset in the osmotic pressure of the plants affects the rate of water intake by plant roots and its subsequent use in the process of photosynthesis. High concentrations of Na^+ in soil therefore affect the metabolism of the plants and this can translate negatively to crop yield (Mohan et al., 2000; Zaidi et al., 2015). Saleh et al. (1999) concluded that excessively high salinity waters also have the tendency to affect the ability of the plants to absorb nutrients and water. Fig. 12 is based on the United States Salinity Laboratory (USSL, 1954), which represents a plot of sodium adsorption ratio (SAR) against EC (salinity).

All the samples from the study area plotted within the "low sodicity" (S1) region and "low to high salinity" ranges (C1 – C3). About 18% of the samples fell within C1– S1 (low salinity—low sodicity) and are mainly composed of waters from cluster 1 members of the Q-mode HCA. Samples from cluster 1 have been categorised as recharge zones, and have low ionic content. Most of the samples (72%) plotted within the C2–S1 region, "medium salinity—low sodicity" irrigation waters, whereas only 6% of the samples plot within C3–S1. All three regions present water of good quality and may be used for irrigation without prior treatment. This assertion is corroborated by the Wilcox (1955) plot, in which all the water samples plot in "excellent to permissible" category.

It is obvious from Figs. 12 and 13 that the salinity of the groundwater in the study area increases as the water travels from recharge (cluster 1) to discharge (cluster 3) areas. Cluster 1 samples are typically low in both sodium and salinity as a result of the short residence time and interaction with the geology. Cluster 2 samples appear to present the best balance of sodium and salinity ranges (SAR = 1–5 and EC = 500–900 μ/cm) (Banoeng-Yakubo et al., 2009) and hence have the best quality for irrigation. But as the groundwater interacts and dissolves the rock matrix, alongside getting polluted by anthropogenic sources such as agrochemicals and domestic wastewaters, its quality for irrigation deteriorates, as seen in cluster 3 samples (Fig. 12).

5. Conclusion

The key factors controlling groundwater chemistry and quality in some Voltaian and Basement aquifers in portions of Sawla-Tuna-Kalba District, northern Ghana have been assessed. Statistical techniques such as HCA, PCA and correlation analysis coupled with conventional hydrochemical plots suggests the dissolution of silicate minerals, particularly feldspars and micas in the rocks, as well as the influence of agrochemicals and domestic waste as the main factors controlling groundwater chemistry in the study area. Even though silicate mineral weathering was identified as the dominant process controlling the groundwater chemical composition, the concentration of SiO_2 is low and did not contribute significantly to the EC. Mineral speciation calculations derived from the analysis also suggests that the most stable silicate mineral phase is kaolinite, which suggests that groundwater in the area is at intermediate stage, and flow is not restricted mainly due to the occurrence and pervasiveness of secondary permeability.

Q-mode HCA identified three (3) groundwater flow regimes in the study area, recharge zones (cluster 1) located in high elevated areas, characterised by low TDS, and dominated by Ca–HCO_3 water type; transition zones (cluster 2) dominated by Mg–Ca–HCO_3 water type; and Ca–Na–K–HCO_3 water type (cluster 3) in discharge areas.

Also, groundwater quality for domestic purposes was assessed using a weighted arithmetic index approach. The computed water quality indices (WQIs) from the data suggest that 94% of the sampled wells provide groundwater of "excellent" quality for drinking purposes, whereas 5% and 1% present water of "good" and "poor" quality respectively. The poor quality presented by some of the wells is attributed to elevated levels of fluoride, arsenic, Fe and TDS and may have resulted from the leaching of such ions into the groundwater. The study also finds groundwater in the area to be permissible for irrigation based on the USSL and Wilcox plots.

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Declaration of competing interest

The authors confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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