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Evolutionary analysis of groundwater flow: Application of multivariate statistical analysis to hydrochemical data in the Densu Basin, Ghana

Sandow Mark Yidana*, Patrick Bawoyobie, Patrick Sakyi, Obed Fiifi Fynn

Department of Earth Science, University of Ghana, Legon, Ghana

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A B S T R A C T

An evolutionary trend has been postulated through the analysis of hydrochemical data of a crystalline rock aquifer system in the Densu Basin, Southern Ghana. Hydrochemcial data from 63 groundwater samples, taken from two main groundwater outlets (Boreholes and hand dug wells) were used to postulate an evolutionary theory for the basin. Sequential factor and hierarchical cluster analysis were used to disintegrate the data into three factors and five clusters (spatial associations). These were used to characterize the controls on groundwater hydrochemistry and its evolution in the terrain. The dissolution of soluble salts and cation exchange processes are the dominant processes controlling groundwater hydrochemistry in the terrain. The trend of evolution of this set of processes follows the pattern of groundwater flow predicted by a calibrated transient groundwater model in the area. The data suggest that anthropogenic activities represent the second most important process in the hydrochemistry. Silicate mineral weathering is the third most important set of processes. Groundwater associations resulting from Q-mode hierarchical cluster analysis indicate an evolutionary pattern consistent with the general groundwater flow pattern in the basin. These key findings are at variance with results of previous investigations and indicate that when carefully done, groundwater hydrochemical data can be very useful for conceptualizing groundwater flow in basins.

1. Introduction

Groundwater hydrochemical data has several utilities in general basin-wide hydrogeological studies. In addition to providing indications on the main processes influencing the general quality, analyses of hydrochemical datasets have been useful in developing preliminary models of regional groundwater flow geometry and are thus crucial in developing conceptual models of groundwater flow at both the local and regional scales. Studies of Garrels and Mackenzie (1967), Toth (1984) and Ophori and Toth (1989) suggest that certain aspects of groundwater quality may be related to the hydraulic regime. In line with this fact, Cloutier et al. (2008) applied multivariate statistical techniques to hydrochemical data and revealed trends of variation that are consistent with the hydraulic theory. Other recent examples are contained in Petrides et al. (2006), Kebede et al. (2008), Zhu et al. (2008), Banoeng-Yakubo et al. (2009), Yidana et al. (2012) among others. In all the above researches, clear links were established between the groundwater flow regime and hydrochemical variations at the local to regional scales and provided preliminary information for understanding general groundwater evolutionary patterns.

Perhaps the commonest conventional approach to hydrochemical data treatment and analysis to reveal such latent characteristics is the application of advanced statistical techniques, which has been copiously used to assist in establishing such regional trends. These analyses lead to other key aspects of the hydrogeology including the determination and ranking of the main sources of variation in the hydrochemistry and the spatial patterns of distribution of such factors (e.g. Mahlknecht et al., 2004; Cloutier et al., 2008; Viero et al., 2009; Yidana et al., 2012). Two main multivariate statistical techniques have been commonly used in these applications: factor analysis and hierarchical cluster analysis. Although advanced statistical techniques do not establish cause and effect relationships, they provide information from which such relationships can be established. The joint application of multivariate statistical techniques, conventional graphical methods (e.g. McNeil et al., 2005), and mass balance modelling (e.g. Ortega-Guerrero, 2003; Andre et al., 2005) in hydrological data analysis has been copiously documented in the literature and has assisted in

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* Corresponding author.
E-mail addresses: smyidana@ug.edu.gh, yidanas117@gmail.com (S.M. Yidana).

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the understanding of flow systems (e.g. Cloutier et al., 2008), and the relative impacts of anthropogenic and natural sources of variation of water quality (e.g. Yidana et al., 2012).

In the Densu Basin, Ghana, groundwater constitutes the most valuable resource for meeting domestic, industrial, and irrigation needs. In recent years, the pressure on the resource has been rising due to increasing population density, growing needs in mechanized agricultural practices, rapid urbanization amongst others (Adomako, 2011). These pressures on the resource are bound to impact on aspects of its quality in addition to the quantity. Additionally, the interaction between groundwater and the aquifer materials through which it moves, undoubtedly changes groundwater hydrochemistry (Acheampong, 1996) and may have implications for its suitability for various uses. It is therefore important to provide an assessment of the relative contributions of natural rock or mineral weathering and other processes on the quality of groundwater for use in the basin. Moreover, a regional assessment of hydrogeology will require information on the general pattern of groundwater flow and evolutionary trends of groundwater quality. Such trends are essential aspects of a decision support system which safeguards the integrity of the resource and also highlight areas of possible concern in terms of resource quality and potability.

This study undertakes a regional assessment of the hydrochemistry and groundwater evolutionary trends in the Densu Basin, Ghana, using a suite of multivariate statistical techniques and conventional graphical methodology. In addition to highlighting the general groundwater flow pattern and spatial hydrochemical facies, this study alleges the main sources of variation in the groundwater quality in the area. It also highlights the spatial variations in the main factors responsible for the hydrochemical evolution of groundwater in the basin. Such studies are very rare in the sub-region especially in the study area. Whereas the general regional hydrochemical facies trends highlight an evolutionary trend consistent with the flow geometry, the factor intensity maps underscore the relative impacts of the various sources of variation in the hydrochemistry and are pioneering in the general hydrochemistry of the basin. Although the application of multivariate statistical methods to hydrochemical data is not new, the utility of such methods in a sequential fashion to predict and conceptualize the groundwater flow geometry is novel and can be applied in other areas to achieve similar results. Adomako et al. (2011) conducted hydrochemical evaluation of the basin using similar techniques. However, the evolutionary trend predicted by their analysis focused on hydrochemical facies and their and their relationships with each other. However, no clear groundwater flow pattern was clearly predicted from their study. In this current study, factor score maps have been generated and compared with a groundwater potentiometric map for the entire basin. The clear agreement between the main processes controlling groundwater hydrochemistry and the general flow pattern in this current study indicates that when properly done, analysis of hydrochemical data can clearly predict groundwater flow geometry and assist in basin-wide conceptual groundwater modelling. This is absent in the analysis of Adomako et al. (2011).

2. The study area

The Densu River Basin (Fig. 1) has a drainage area of approximately 2564 km^2, and is characterized by an undulating topography (Adomako et al., 2011). The Densu River system is predominantly recharged by inflows from the Atewa-Atwiredu hills in the East Akim District of the Eastern Region of Ghana, and flows down south (WRC, 2012) into the sea. It is boarded to the east and north by the Odaw and Volta Basins, respectively. In the northwest and west of the Densu Basin are Birim, Ayensu and Okrudu basins respectively (WRC, 2012). The major rainy season occurs from April/May to July, reaching its peak in June when the maritime instability causes a surge of the moist south-westerly air stream resulting in the intensification of the monsoon rain (Junner and Hirst, 1946). The minor rainy season in the area occurs between September and November (Adomako et al., 2011). On the basis of several years of monitored data, the average total annual rainfall ranges from 1700 mm in the wet interior to 800 mm in the dry equatorial zone near the coast (Adomako et al., 2011). The mean annual temperature is 27 °C, with March/April being the hottest (32 °C) and August is the coolest (23 °C). The maximum and minimum relative humidity values vary from 89% to 93% and 41–72%, respectively (Water Resources Commission, 2012).

The Densu Basin is underlain predominantly by the basin type granitoids (Cape Coast Granites) which underlie over 90% of the area (Junner and Hirst, 1946). Rocks of the Birimian metavolcanics and sediments underlie the northwestern parts of the terrain, while quartzites, schists and phyllites of the Togo Structural unit underlie the southeastern parts, constituting about 6% of the total landmass of the basin. The hydrogeological conditions of rocks of the basin are based on the occurrence and pervasiveness of secondary structural entities in the forms of joints and weathered zones which create ingresses for groundwater recharge, flow, and storage. Therefore, the hydrogeological properties do not present continuously uniform characteristics. Analysis of borehole data in the basin suggests that borehole depths vary from 9.1 m to 103.0 m in the granites, 23.0–40.0 m in the Birimian and 28.0 m–97.0 m in the Togo Structural Unit (Adomako et al., 2011). The weathered zone varies in thickness from 1.0 m to 32.0 m, 5.0 m–27.0 m and 3.0 m–36.0 m in the granites, Birimian and Togo rocks, respectively (Adomako et al., 2011). The data suggests that static water level is in the range of 0.1–13.5 m, 0.8–16.9 m, and 1.1–17.9 m respectively in the granites, Birimian and Togo rocks. Borehole yields are highly variable and lie in the range of 0.1 m^3 h^{-1} - 30.0 m^3 h^{-1} with mean value of 2.0 m^3 h^{-1} in the granites. In the Togo unit and Birimian formations borehole yields are within 0.6 m^3 h^{-1}- 6.0 m^3 h^{-1} and 0.7 m^3 h^{-1} - 9.0 m^3 h^{-1} with the mean values of 2.8 m^3 h^{-1} and 3.7 m^3 h^{-1} respectively (Adomako et al., 2011).

3. Methodology

3.1. Field observations and sampling

The sampling campaign was undertaken between December 2014 and January 2015 during which groundwater outlets in the basin were sampled, following standard sampling protocols as suggested in Appelo and Postma (2005). A total of 63 groundwater outlets were sampled; 57 samples from boreholes, 6 from hand dug wells. Prior to sampling, all the groundwater outlets were sufficiently purged to ensure that representative samples were taken. Samples were subsequently filtered through 0.45 μm membranes and collected in 500 mL acid washed, well rinsed polyethylene bottles. Samples for major cations were filtered and acidified with nitric acid (HNO_3); samples for analysis of anions were filtered but were not acidified. At each site, four samples were collected and properly labelled as ‘cations’, ‘anions’, ‘silica’, ‘Dissolved Oxygen (DO)’. Samples for DO were preserved through the addition of Manganese (II) Sulfate. The EC, Total Dissolved Solids, TDS, Temperature, and pH were measured onsite with the help of a portable pH-EC meter. All samples were preserved in ice chests within which temperatures had been reduced to 4 °C to discourage reactions and bacterial action whilst samples were in transit to the laboratory.

Geographical coordinates of every sampled location were taken using global positioning system (GPS). A water sample location map

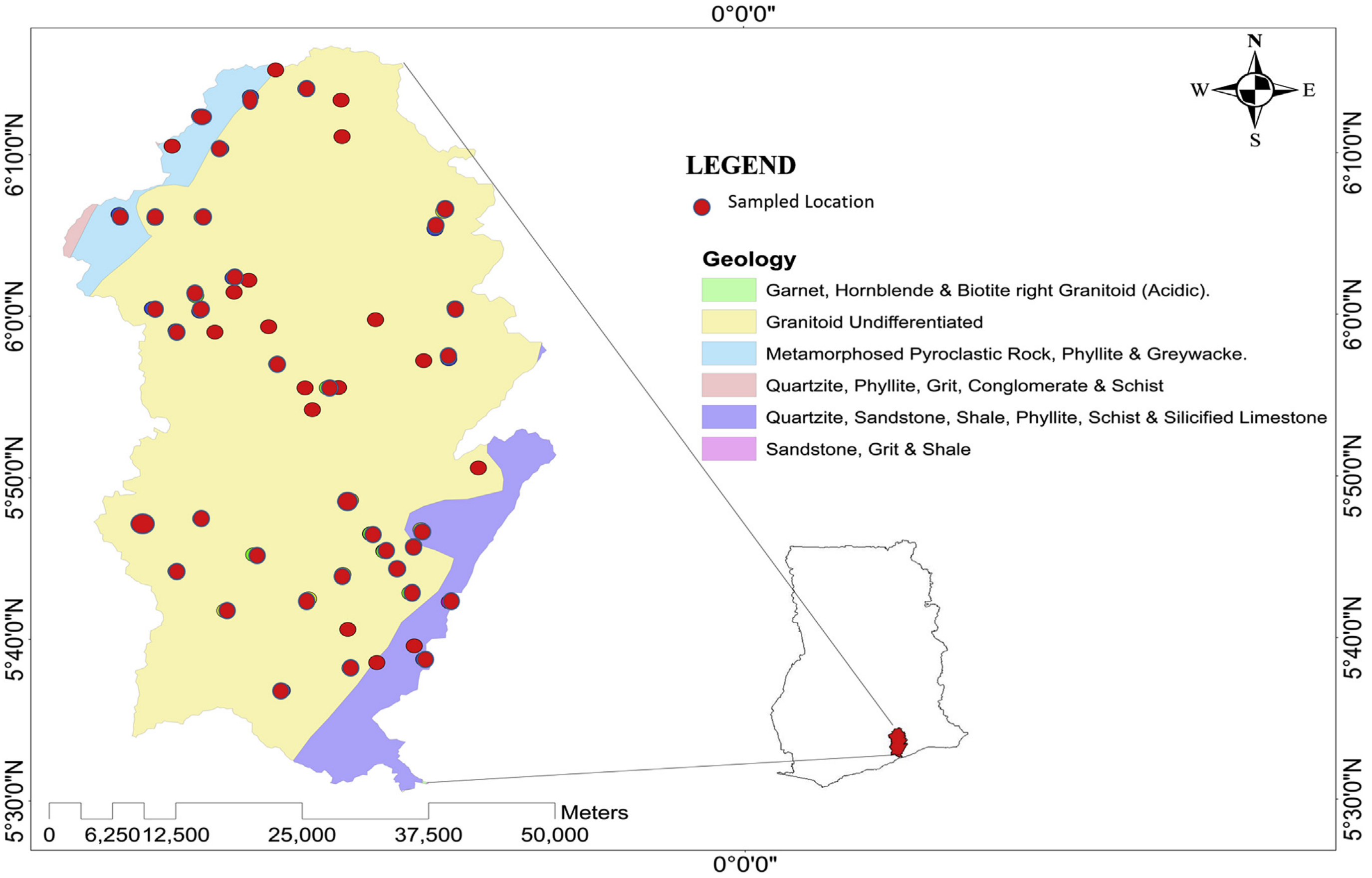

Fig. 1. A map of the Densu Basin showing the geology and sampled locations.

was generated from the GPS location recorded (Fig. 1).

3.2. Laboratory analysis

All the samples were taken to the analytical laboratory of the Ghana Atomic Energy Commission (GAEC) in Kwabenya, Accra for analysis. Major ions such as Sodium (Na^+) and Potassium (K^+) were analyzed in the laboratory using the flame photometer (Sherwood model 420 with detection limit of 0.001). Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) were analyzed using the AA240FS Fast Sequential Atomic Absorption Spectrometer. The ICS-90 Ion Chromatograph (DIONEX ICS-90) was used for the analysis of Chloride (Cl^-), Fluoride (F^-), Nitrate (NO_3^-), and Sulfate (SO_4^{2-}). Phosphate (PO_4^{3-}) was determined by the ascorbic acid method using the ultraviolet spectrophotometer (UV-1201). Silica analysis was also carried out using Spectrophotometric Silicamolybdate Method at the Council for Scientific and Industrial Research (CSIR) while the Dissolved Oxygen (DO) was measured using the Winkler method, at the GAEC Environmental Chemistry Laboratory in Accra, Ghana.

3.3. Multivariate statistical modeling

The hydrochemical data from the laboratory analysis of the samples were subjected to internal consistency tests. The Chemical Balance Error, CBE (Equation (1)) was applied for that test. It is conventional practice to use charges (cation and anion balance) in water samples as a measure of internal consistency. Normally, the cations and anions should exactly balance, and under ideal conditions where the analysis recovers most of the parameters, the cations and anions should not differ by more than 5% (Appelo and Postma, 2005).

$$CBE = \frac{\sum Cations - \sum Anions}{\sum Cations + \sum Anions} \times 100\% \tag{1}$$

Where all concentrations of cations and anions are in meq/L.

In addition to the CBE, concentrations of specific ions in comparison with the total dissolved ion content, the consistency between parameters (pH, EC, TDS) measured in the field and those measured in the laboratory were all used to assist in determining internal consistency of the hydrochemical data. For instance, for each sample, the TDS content was checked by adding up the concentrations of the major ions. These values were compared to the TDS values measured in the field with portable equipment. These parameters all suggest that the data is largely internally consistent and could be used for further processing.

Multivariate statistical techniques were applied to the datasets after they had been log-transformed to meet or approximate the requirements of normal distribution for optimal results in multivariate statistical analysis. Factor analysis was applied to the log-transformed dataset to reveal the latent characteristics inherent in them. Factor analysis, with principal components as the extraction procedure, was applied to the log-transformed datasets of all the parameters. In the extraction process of the principal components (PCs), parameter communalities were used to limit the number of variables that are significant contributors to the final factor model. The criterion was based on variables with communalities equal to or greater than 0.5 so that variables with communalities <0.5 were dropped out of the process as they would have been regarded as redundant variables. In the determination of the most appropriate number of factors in the eventual model, the Kaiser (1960) criterion was used. This criterion ensures that factors with eigenvalues lower than 1.0 are sieved out because a worthy factor should able to account for the variance of at least one variable in the entire analysis. The PCs were rotated using varimax rotation. The variables which made it to the final model were used to generate a full factor model comprising 9 PCs. Q-mode HCA was then performed on the factor scores of the 9 factors resulting from this process. The significance of this procedure lies in the fact that redundant variables do not form part of the process of determining the spatial pattern of variability in the causative factors of the general hydrochemistry. In performing the Q-mode HCA, Squared Euclidean Distances were used as the measure of similarity/dissimilarity whereas the Ward's linkage was used to link up initial clusters. All the statistical analyses were performed in the IBM Statistical Package for Social Scientists, IBM SPSS, version 20 (IBM, http://www-01.ibm.com/software/analytics/spss/).

4. Results and discussions

4.1. General hydrochemistry and parameter concentration ranges

The concentration ranges of the various parameters analyzed from the samples are presented in Fig. 2. The pH of groundwater in the basin ranges from 5.54 to 7.87 with a mean and standard deviation of 6.83 and 0.53 pH units respectively. The pH data appears to be largely homogeneous, displaying little variability over the domain of the study area. Less than 25% of the samples present pH values lower than 6.5 but higher than 6.0 (Fig. 2a) while over 75% are well within the WHO (1996, 2004) standard for drinking water. The range of variation in the pH is also consistent with observations within similar lithologies in other parts of the country, especially within the granitoids (e.g. Yidana, 2011). Adomako (2011) suggests that slightly acidic waters in the basin could be due to excessive use of ammonia and manure as fertilizers from farming activities in the study area. The TDS values range between 460 mg/L and 2800 mg/L with a mean of 1100 mg/L. More than 50% of groundwater samples in the area appear to present TDS values above 1000 mg/L but below 1500 mg/L. These observed TDS values may arise from a combination of factors including mineral weathering and anthropogenic activities.

Sodium (Na^{+}) appears to be the most abundant cation in the study area (Fig. 2b) but the data suggests that in much of the area Na^{+} concentration is lower than the WHO (1996, 2004) recommended maximum limit of 200 mg/L for domestic purposes. The distribution suggests a high degree of dispersion in the data of the Na^{+} ion compared to the other cations in the area. The apparently high degree of dispersion in the Na^{+} ion concentration may suggest a variety of geogenic and anthropogenic sources, which will certainly vary in the space of the domain. The K^{+} ion displays a similar trend of variability, which is quite higher than that observed for the alkaline earth elements analysed in this study (Ca^{2+}, Mg^{2+}). This may suggest that the possible sources of variation in the concentrations of the alkali elements (Na^{+}, K^{+}) are quite variable compared to Ca^{2+}and Mg^{2+} in the terrain. The dominance of Na^{+} over Ca^{2+}and Mg^{2+} may also be related to ion exchange processes in the saturated and unsaturated zones. Sorption sites generally have preference for the ions with relatively higher charge density and as such the alkaline earth elements are often preferred to alkali elements (Fetter, 1990). The observed concentration ranges may therefore be partly related to the evolutionary trend of groundwater through the unsaturated zone and its transitioning along flow lines in the domain. The preference of Ca^{2+} and Mg^{2+} as against Na^{+} by sorption sites may have led to the selective exchange of Na^{+} for Ca^{2+} and Mg^{2+}, leading to the relative high abundance of the former over the latter in solution in groundwater. This evolutionary trend is supported by the Chebotarev (1955) sequence as exemplified in Ophori and Toth (1989).

The HCO$_3^-$ ion appears to be the most abundant anion in the study area. It also presents an apparent homogeneity in its data distribution compared to the other anions. This indicates that the processes leading to the loading of this ion in groundwater in the area are not as variable as the other hydrochemical parameters. This is because the relatively low variance suggested by the relatively smaller box indicates similarity among the HCO$_3^-$ data from the various sampled locations. The dominance of the HCO$_3^-$ ion also suggests that groundwater in the area is generally young to intermediate groundwater types. This is consistent with the Chebotarev (1955) sequence which suggests the preponderance of HCO$_3^-$ ion in recharge-dominated areas. Chloride and SO$_4^{2-}$ present the most variable datasets and may have resulted from significant anthropogenic contributions. Generally in the groundwater evolutionary sequence, discharge areas are dominated by SO$_4^{2-}$ and Cl^{-} anions (Ophori and Toth, 1989). The data ranges presented by the anions suggest concentrations which are largely within acceptable ranges for most domestic purposes in the terrain.

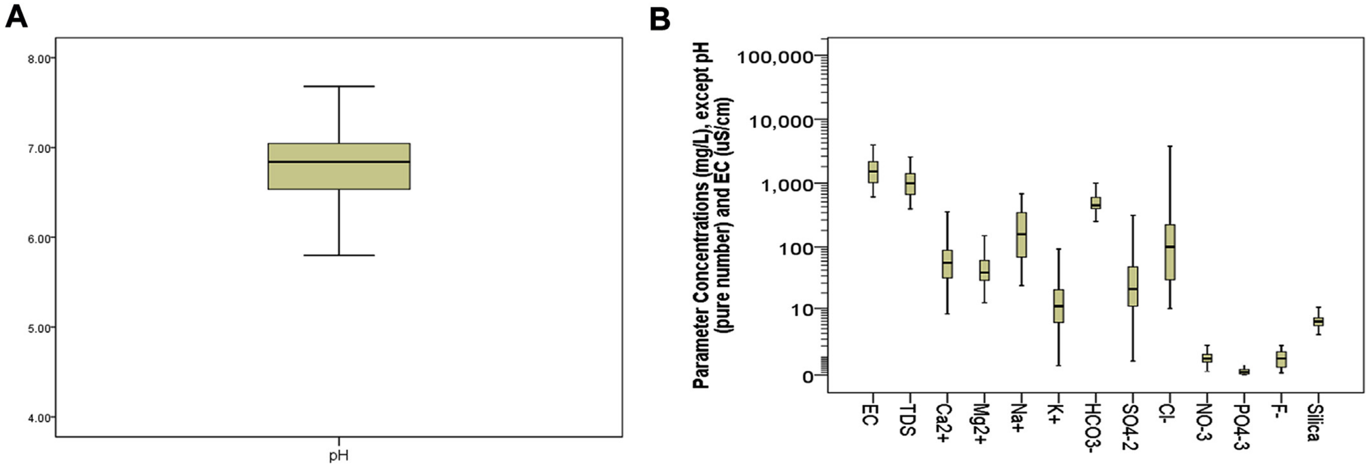

Fig. 2. Box-and-Whisker plots showing the summaries of the main parameters used for this study.

4.2. Sources of variation and the reactive mineralogy of the terrain

The final factor model generated from the hydrochemcial datasets is presented in Table 1. It consists of three factors, which account for 77.5% of the total variance in the hydrochemistry. It is also obvious in Table 1, that the model does not contain Ca^{2+}, Mg^{2+}, and K^{+}. This is because after a series of successive runs, these ions consistently presented low communalities and therefore were not considered significant enough contributors to the factor model. They were therefore dropped out of the final analyses. Factor 1 has significant positive loadings for EC and all the major ions. It is also clear from Table 1 that factor 1 alone accounts for over 48% of the total variance in the hydrochemistry and thus represents a significant set of processes controlling groundwater hydrochemistry. Unfortunately, there is a poor negative correlation between factor 1 and silica, suggesting that the process or set of processes encapsulated in factor 1, does not have a bearing on the concentrations of silica in the terrain. Thus, silicate mineral weathering may not be the most important geochemical process controlling hydrochemical data variation in the Densu Basin, although the underlying geological conditions favour the dominance of silicate minerals. However, all the major parameters correlate positively with factor 1, suggesting the dissolution of other relatively more soluble minerals in the saturated and unsaturated zones. Although NO_3^- presents a low correlation under this factor, the negative correlation is indicative of processes in the unsaturated zone which have an adverse impact on the concentration of NO_3^-. It appears from the entire factor model that HCO_3^- and NO_3^- consistently correlate negatively with each other, indicating probable organic matter oxidation to inorganic carbon in the unsaturated zone using NO_3^- as the main oxidizing agent. This may indicate that unsaturated zone processes, including the dissolution and leaching of ions by infiltrating rainwater through the unsaturated zone, are the most important processes controlling groundwater hydrochemistry in the area. The observed dominance of Na^{+} over Ca^{2+} and Mg^{2+} in the terrain may be associated with ion exchange processes in the unsaturated zone during the infiltration and percolation of rainwater into the saturated zone. Salifu et al. (2013) made a similar observation in parts of northern Ghana when they undertook analysis of the geochemistry of porewater in comparison with groundwater. The positive correlation of F^{-} with factor 1 suggests that such unsaturated zone processes are significant in influencing the concentration of this ion in the saturated zone.

This hypothesis appears to be supported by a Gibbs (1970) diagram produced from the hydrochemical dataset of the main cations and TDS in the study area. Fig. 4 illustrates the position of the data, suggesting the dominance of a geogenic sources in the variation in the hydrochemistry. It is also obvious from Fig. 3, that some of the samples plot within the evaporation/seawater dominated areas, indicating the impact of evaporative enrichment of the various ions in the unsaturated zone. In addition, most of the samples within the geogenic region of Fig. 3 plot close to the boundary with the region dominated by evaporation processes. The underlying geology is dominated by rocks rich in silicate minerals. Drever (1988, Drever and Marion, 1998) and Appelo and Postma (2005) suggest that silicate mineral weathering is a slow process requiring several years to register significant impacts on the hydrochemistry of groundwater. In addition, the factor model does not appear to support silicate mineral weathering as the main source of significant variation in groundwater hydrochemistry. The dissolution of soluble salts such as chlorides, sulphates, carbonates and other minerals in the unsaturated zone by rainwater in transit, and cation exchange processes may be the dominant process suggested by the factor model. Factor 1 is therefore a mixed factor comprising two main geogenic processes: dissolution of soluble minerals in the unsaturated zone and cation exchange.

Table 1
Factor model for the study area.

	Component		
	1	2	3
pH	0.272	**0.829**	0.162
EC	**0.952**	-0.167	-0.057
Na^{+}	**0.821**	0.133	-0.206
HCO_3^-	**0.732**	-0.473	-0.052
SO_4^{2-}	**0.790**	0.014	-0.179
Cl^{-}	**0.874**	-0.009	0.098
NO_3^-	-0.388	**0.771**	-0.197
F^{-}	**0.674**	-0.028	-0.463
SiO_2	-0.127	0.010	**0.925**
Eigenvalue	**4.406**	**1.491**	**1.080**
% Variance Explained	**48.954**	**16.566**	**11.995**

The bold texts represent high factor loadings (that is, loadings higher than or equal to the absolute value of 0.5).

An evaluation of the role of ion exchange processes in modulating the relative concentrations of the alkali and alkaline earth elements, especially in the unsaturated zone, was evaluated using a biplot of $Ca + Mg-SO_4-HCO_3$ against Na-Cl in meq/L. As suggested by Jalali (2007) and Yidana and Yidana (2010), these indices respectively refer to the sum of alkaline earth and alkali elements originating from a source other than their respective sulfates, carbonates and chlorides. If an inverse relationship is achieved in such a plot and a slope of -1 is attained with most of the data plotting close to the origin, cation exchange is suggested. Fig. 4a provides such a plot for data in the study area, and appears to affirm the importance of cation exchange processes in the hydrochemistry of groundwater. The indication is that Ca^{2+} and Mg^{2+} are being preferentially adsorbed onto cation exchange sites which in turn release Na^{+} ion into the groundwater system. This accounts for the relatively higher concentration of Na^{+} when compared to Ca^{2+} and Mg^{2+} in the groundwater system. The impact of cation exchange on the hydrochemistry of groundwater in the basin is corroborated by the biplots for $Ca-HCO_3$ and $Mg-HCO_3$ in Fig. 4b. A plot of Ca^{2+} against HCO_3^- presents an opportunity to determine whether the probable sources of variation in the hydrochemistry of

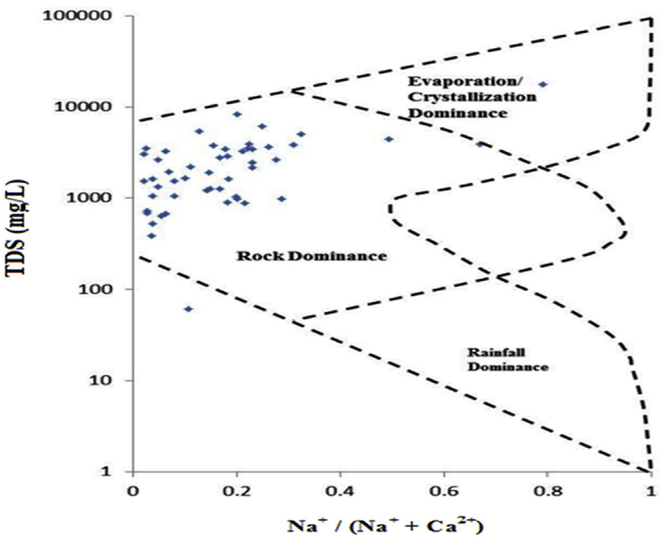

Fig. 3. Gibbs plot showing the main factors responsible for the hydrochemical variations in the study area.

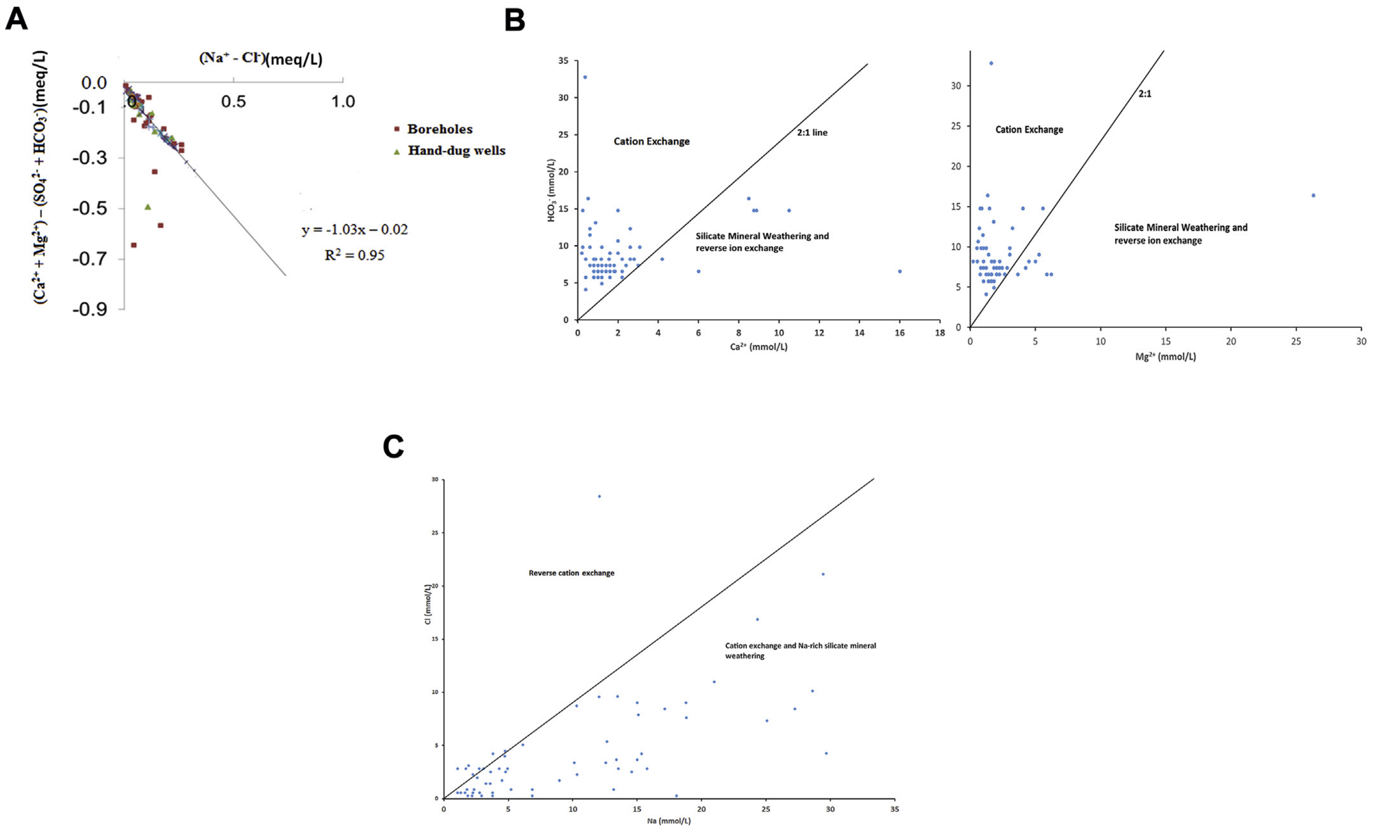

Fig. 4. a. A Ca + Mg-SO_4-HCO_3/Na + K-Cl biplot to assess the role of cation exchange in the hydrochemistry of the basin. b.A Ca/HCO_3 biplot to assess the role of cation exchange in the hydrochemistry of the basin. c A Na/Cl biplot to assess the role of cation exchange in the hydrochemistry of the basin.

groundwater in the area. The main sources of Ca^{2+} and HCO_3^- in groundwater are the dissolution carbonate minerals and incongruent silicate mineral weathering. The dissolution of calcite for instance leads to the generation of Ca^{2+} and HCO_3^- in the ratio of 1:2. Thus, if calcite is the main source of these two ions, a linear plot will have all the data along the 1:2 line. If the data falls on the HCO_3^- side of the line, it suggests cation exchange activity whereby Ca^{2+} is preferentially adsorbed onto exchange sites, leading to a reduction in the concentration of the same ion in solution in water. As indicated in Fig. 4b, the data suggests cation exchange activity, and corroborates the indications of Fig. 4a and the interpretation of factor 1. This is closely supported by Fig. 4c which has a plot of Na^+ against Cl^-.

A factor score map for factor 1 (Fig. 5a) shows a clear distinction between the northern and southern parts of the terrain. High factor scores are associated with the southern parts, with the lowest scores in the northern and middle sections of the domain. The factor scores do not appear to be consistent with the underlying geology, suggesting that the contribution of the host, silicate mineral rich geology is not the main source of variation in the hydrochemistry. The apparent increase in the impacts of factor 1 from the northern to southern parts of the terrain may be attributed to a general evolution from the northern high topographical elevation, recharge areas to the low lying, southern parts which are characteristically groundwater discharge areas where the general flow is towards the sea. Fig. 5b is a groundwater potentiometric map of the study area. It is a modified form of the figure generated by Yidana et al. (2014) from the calibration of a transient model over the terrain. It is obvious in this figure that there's a general north-south groundwater flow pattern in the basin. The hydrochemical evolution suggested by the factor score pattern of distribution therefore appears to be consistent with the general groundwater flow pattern. It is consistent with the theory of soluble mineral dissolution as the impact of this factor increases from the presume recharge areas (high hydraulic potential areas) to recharge areas (low hydraulic potential zones).

Factor 2 has high positive loadings for NO_3^- and pH, and appears to indicate the effects of manure and other fertilizers used on farms in the area. Factor 2 is therefore an indication of anthropogenic processes, representing the set of anthropogenic activities which contribute to the NO_3^- content of groundwater in the basin. This is because NO_3^- is a nutrient resulting mainly from anthropogenic activities. Agriculture is the main economic activity in the basin and manure and other NO_3^- containing substances are used to enhance crop yield. The impacts of factor 2 (Fig. 5c) appear to be isolated, and highest in areas where farming activities appear to be more intense with the use of fertilizers and manures on farms. There are also obvious high scores in the southern, relatively highly populated areas where the influence of domestic waste and sewerage may be the main source of the high NO_3^-.

The third factor (Factor 3) has high positive loading with silica, indicating that silicate mineral weathering is the third most important process controlling groundwater hydrochemistry. This is due to the fact that the main silicate minerals in the area are largely low temperature feldspars which are resistant to chemical weathering within the regular groundwater temperatures. Longer residence times are required for silicate mineral weathering to provide enhanced contribution to groundwater hydrochemistry (Drever, 1988) in the terrain. The spatial distribution of factor scores for factor 3 (Fig. 5d) indicates that factor 3 is not a significant process in the hydrochemistry of groundwater in the area as the predicted factor scores are generally low. The implication is that silicate

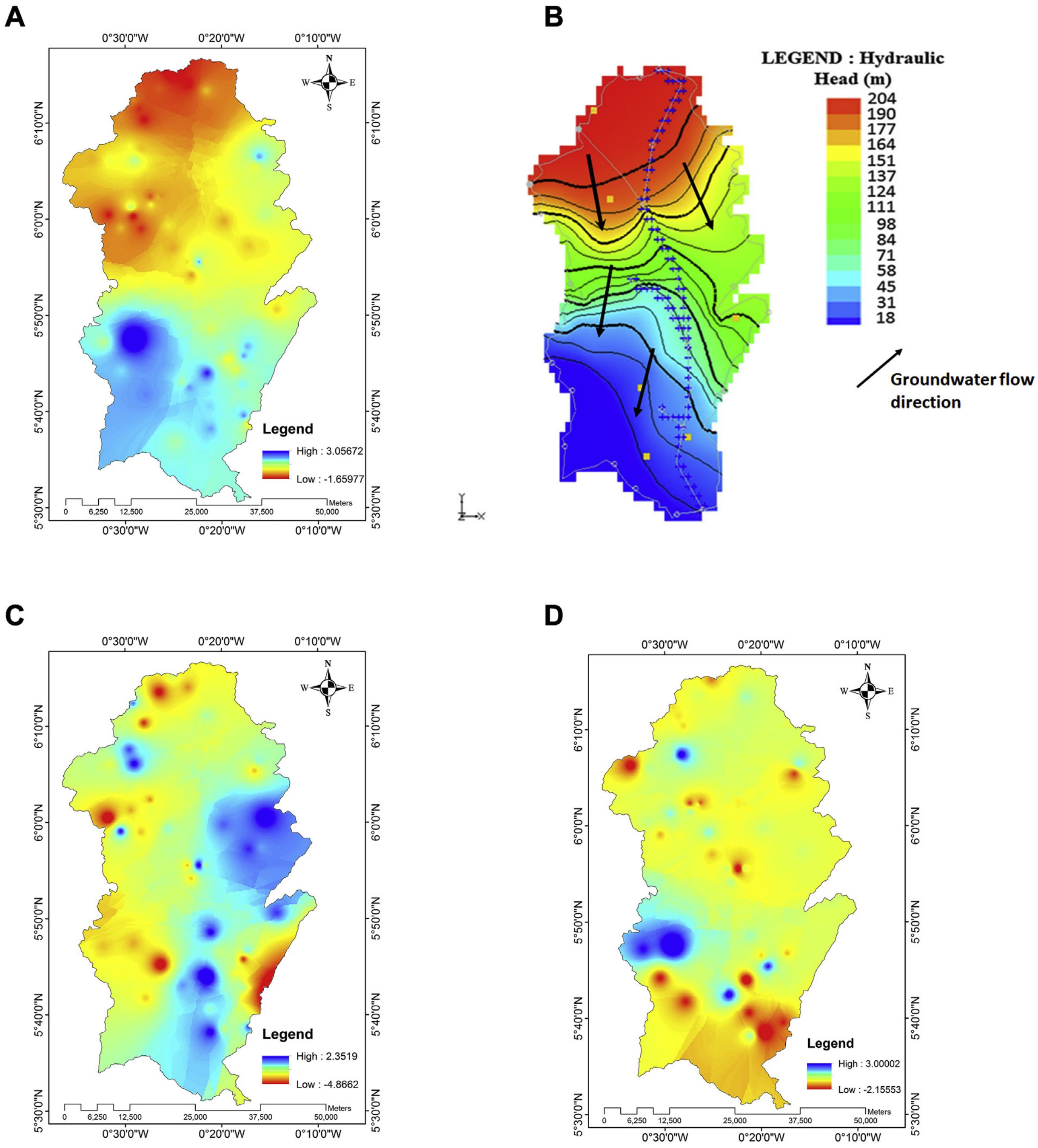

Fig. 5. a. Factor score distribution map for factor 1 (component 1) in the study area. b A groundwater potentiometric map for the Densu Basin (modified from Yidana et al., 2014). c.Factor score distribution map for factor 2 (component 2) in the study area. d.Factor score distribution map for factor 3 (component 3) in the study area.

mineral weathering has not been a pervasive process which influences groundwater hydrochemistry in the area. The isolated areas of high scores are within the granitoid areas, which generally provide indications of some level of contribution of the silicate mineral weathering.

4.3. Spatial groundwater types in the study area

The Q-mode HCA resulted in five main clusters, representing five major spatial groundwater facies in the area. Fig. 6 presents the dendrogram from the Q-mode HCA illustrating the five clusters. In cluster analysis, the choice of the number of clusters in the dendrogram to represent the spatial associations is a semi-objective process. It's usually based on the linkage distance and the researcher's semi-objective impression of how many spatial associations are deemed appropriate. A line (imaginary) is drawn across the dendrogram at a particular linkage distance to determine the number of unique clusters or groups. There are no rules governing the position of this line (‘phenon line’). One can move the phenon line up or down the dendrogram to decrease or increase the number of clusters/groups. In this research, the phenon line was drawn across the dendrogram at a critical linkage distance of 17. Fig. 7 presents the statistical summaries of the parameters within each of the groups. It is obvious that the groups are

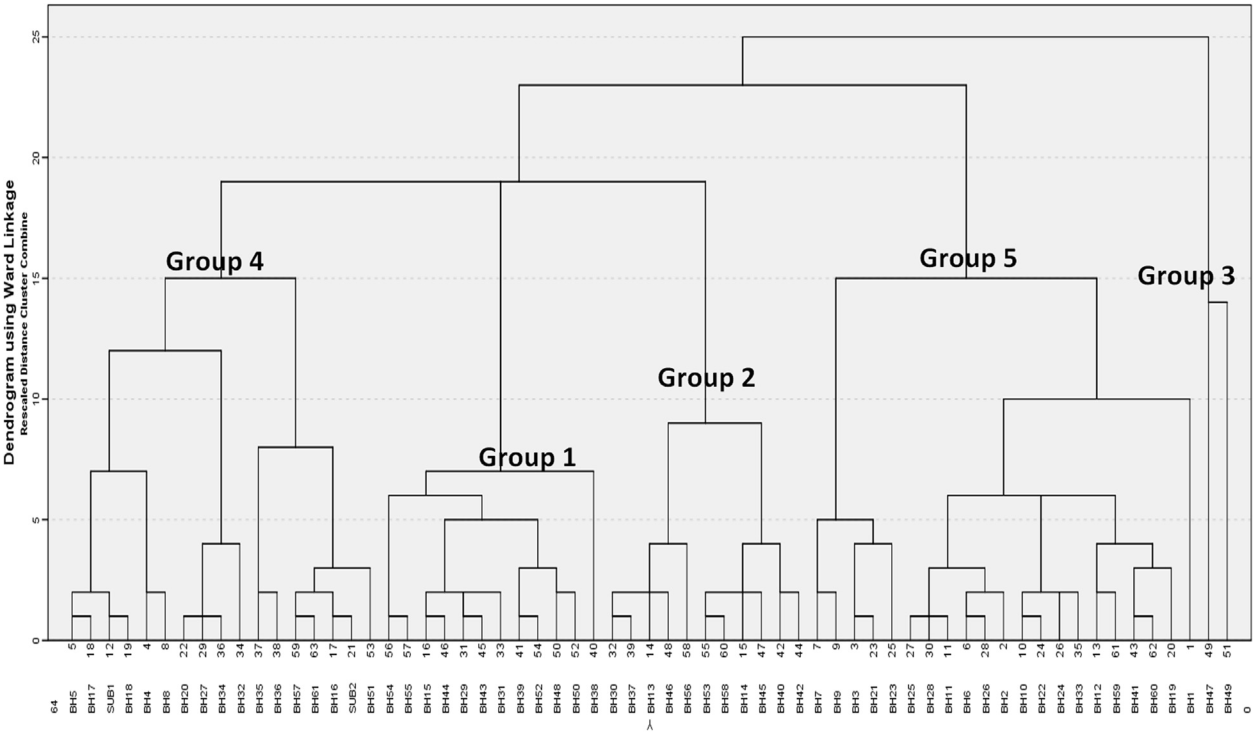

Fig. 6. A dendrogram resulting from the Q-mode HCA.

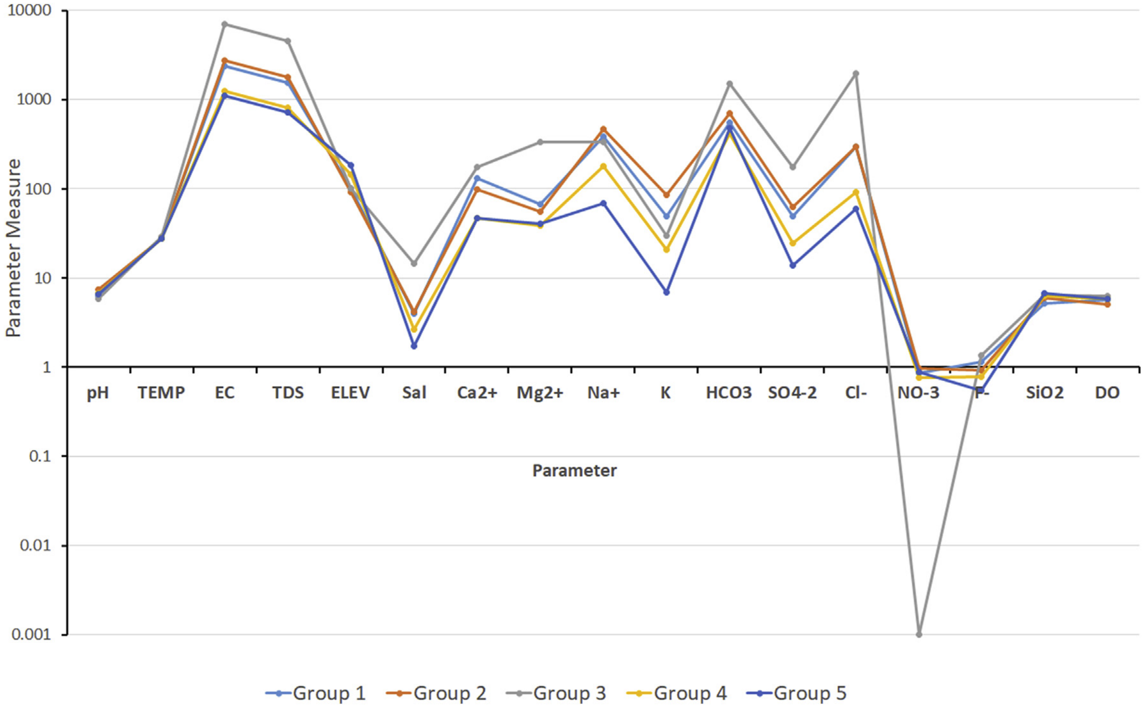

Fig. 7. A plot showing summaries of the concentrations of the main parameters characterizing the five groups distinguished by the Q-mode HCA.

distinguished on the basis of their positions in the general groundwater flow regime. Group 5 members have the highest average elevation, and are also characterized by the lowest measures of almost all the physico-chemical parameters.

Group 5 therefore represents the freshest groundwater types in the area. In addition, as these group members are located in the highest elevations (182 m above mean sea level), they represent recharge areas in the groundwater flow regime. Both the high elevations and the observed low average concentrations of the physico-chemical parameters are consistent with the characteristics of groundwater recharge areas in the flow regime. Conversely, Group 3 presents samples from boreholes with the highest concentrations of most of the physico-chemical parameters (Fig. 7). These are also areas of the lowest elevations, consistent with discharge areas in the general groundwater flow regime. Group 4 follows next after Group 5, presenting generally groundwater with some of the lowest concentrations most of the physico-chemical parameters. The average elevation of Group 4 members is 145 m, which is the next highest elevation after Group 5. It is also obvious from Fig. 8 that Group 5 members are Mg-HCO_3 water types, which transition into Mg-Cl groundwater types in Group 3. Groups 1, 2, and 4 are Na-HCO_3 water types characteristic of intermediate water types in the groundwater flow regime. The spatial pattern of distribution of the samples that form part of the various groups (Fig. 8) indicates that majority of the members of Groups 4 and 5 (generally recharge type groundwater) are clustered in the relatively topographically higher northern parts of the terrain, which happen to be areas of the lowest scores of factor 1 (Fig. 5a). On the other hand, Groups 1, 2, and 3 generally plot towards the low lying southern parts of the terrain where there is a general tendency of flow towards the Gulf of Guinea in the south (Fig. 5b). The results of the cluster analysis therefore adequately predict the expected groundwater flow pattern in the terrain. This prediction is perfectly in line with the general groundwater flow pattern produced from the calibration of a transient state groundwater flow model in the area (Yidana et al., 2014). This amply suggests that careful application of multivariate statistical techniques to hydrochemical datasets is an asset in the initial conceptualization of the general groundwater flow pattern in a terrain.

5. Summary and conclusions

This study has demonstrated the utility of advanced multivariate applications in adequately predicting the general groundwater flow pattern and evolutionary trend as part of basin-wide hydrogeological investigations. Hierarchical cluster analysis has been successfully used, in conjunction with factor analysis, to adequately predict groundwater evolution and its flow pattern in the Densu Basin. The predicted flow pattern is in tandem with groundwater flow pattern predicted by a calibrated groundwater flow model over the terrain. This exemplifies the predictive capacity of factor analysis and HCA, and demonstrates their joint utility in the initial conceptualization of groundwater flow pattern prior to numerical modelling. In the specific case of the Densu Basin, the application of these techniques to hydrochemical data suggests the dominance of three factors in the hydrochemistry: unsaturated zone processes including the oxidation of organic carbon to inorganic carbon as well as the dissolution of soluble salts; the impacts of anthropogenic activities including agricultural chemicals and domestic waste disposal; and silicate mineral weathering. Factor score maps suggest a probable evolutionary theory whereby groundwater transitions from relatively low salinity, Mg-HCO_3 groundwater

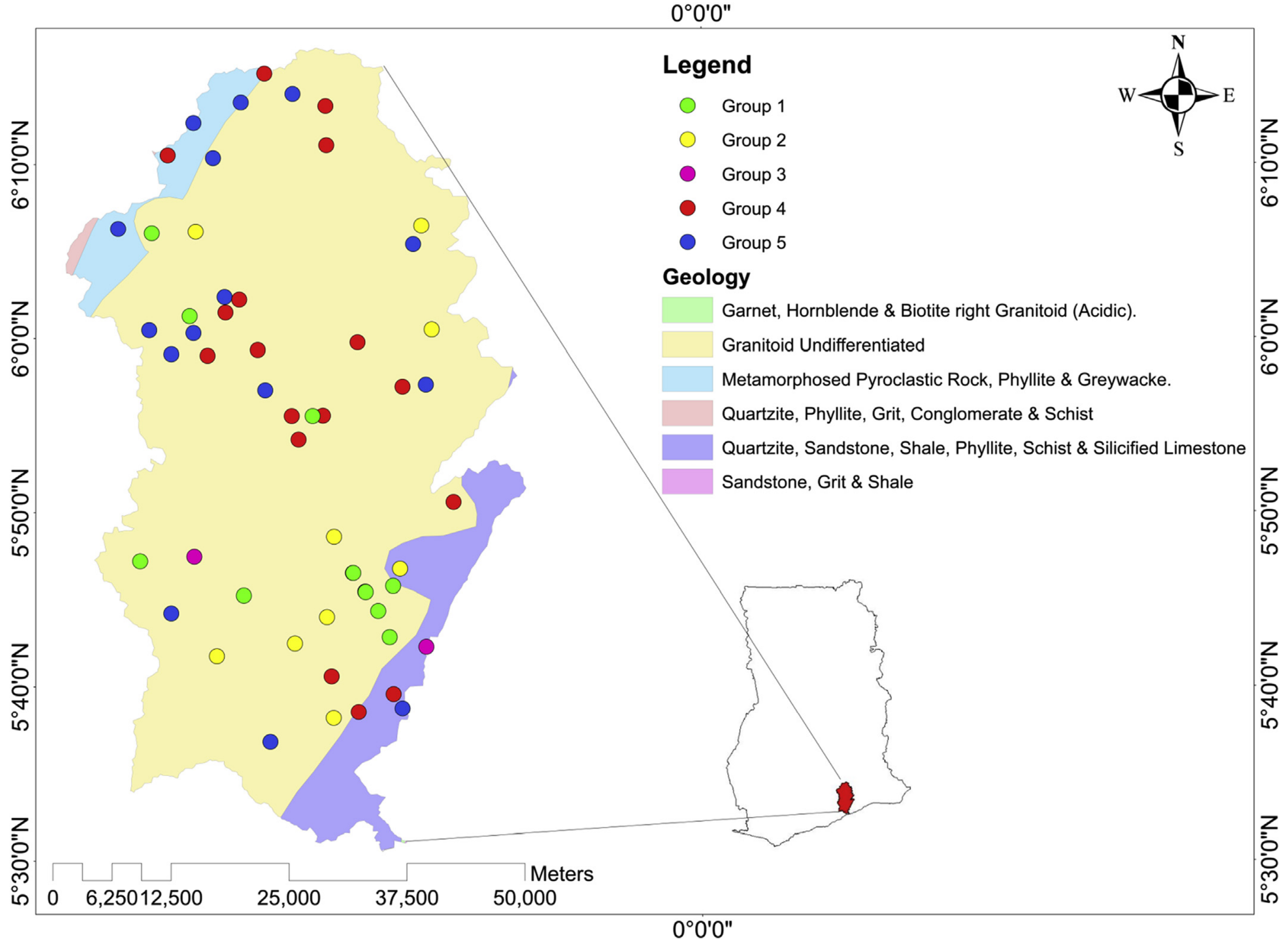

Fig. 8. The distribution of the membership of the five groups distinguished by the Q-mode HCA.

types in the northern, high elevation areas, to high salinity, Mg-Cl water types in the low lying areas, as it flows seaward. The analysis suggests that unlike other parts of the country where silicate mineral weathering is a dominant process in the hydrochemistry of groundwater, the process ranks third in the Densu Basin. Spatial groundwater associations developed through hierarchical clustering are aligned in a fashion akin to the evolutionary trend predicted by the factor scores. The implication of this current investigation suggests that the unsaturated zone plays a very significant role in both recharge and groundwater hydrochemistry in the terrain. Contamination of unsaturated zone material through the disposal of hazardous material on the surface will certainly impact the quality of groundwater in the domain in the long term. The comparatively lower impact of silicate mineral weathering is consistent with an assertion of low residence times of groundwater in the terrain.

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