Available online at www.elixirpublishers.com (Elixir International Journal)

Geoscience

Elixir Geoscience 50 (2012) 10279-10288



Major ion chemistry and identification of hydrogeochemical processes of groundwater in the Accra Plains E.T.Glover^{1,2}, T.T.Akiti² and S. Osae¹

¹National Nuclear Research Institute, Ghana Atomic Energy Commission, P.O. Box LG 80, Legon. ²Graduate School of Nuclear and Allied Sciences, University of Ghana, Atomic Campus.

|--|

Article history: Received: 10 July 2012; Received in revised form: 16 August 2012; Accepted: 30 August 2012;

Keywords

Groundwater, Hydrogeochemical processes, Major ions, Hierarchical cluster analysis.

ABSTRACT

Major ion geochemistry was used to characterize the chemical composition of the groundwater in the Accra Plains and to understand its geochemical evolution. Sodium and chloride were the dominant ions in the groundwater. The TDS values increase south eastwards through the central part of the Plains towards the coast. Three hydrochemicsl facies which evolves from Na-Mg-Ca-Cl-HCO3 to Na-Ca-Cl was identified using the Piper diagram and Chadha proposed rectangular plot. The R-mode factor analysis result show that three factors account for 83.65% of the total variance in the hydrochemistry. Interpretation of the hydrochemical data suggested that mineral (silicate) weathering, cation-exchange and reverse ion-exchange control the chemical composition of the groundwater. The thermodynamic plots indicate that the groundwater is in equilibrium with kaolinite and montmorillonite minerals. The saturation index also indicated that about 47% of the groundwater samples were oversaturated with respect to calcite and dolomite.

processes can be determined.

at different points, an understanding of the geochemical

evolution of these groundwaters and the dominant geochemical

considered as one of the suitable host rocks of radioactive waste

repositories. As such, a number of hydrogeochemical

investigations of granite and gneiss areas are being carried out to

determine their suitable for a radioactive wastes repository (Frape et al, 1984, Nordstrom et al., 1985). The

hydrogeochemical studies include the chemical evolution of groundwater and water-rock interaction in the crystalline rocks.

The purpose of the study was to characterize the chemical

composition and the geochemical evolution of the groundwater

from existing boreholes at different depths and locations in the

and longitude 0° 20' west and 0° 40' east of the Greenwich

meridian. It covers an area of approximately 7000 km². The

area is bounded on the west and the northwest by the Akwapim

Togo Mountains and in the north to the east by the Volta River.

The Accra Plains is located in the south eastern part of Ghana between latitude 5° 30' and 6° 15' North of the equator

Crystalline rocks such as granite and gneiss have been

© 2012 Elixir All rights reserved.

Introduction

The concept of geological disposal of radioactive waste involves isolating the waste from the human environment for long periods, until it presents no significant hazard to human health and the environment (Chapman and McCombie, 2003). Understanding the flow and composition of groundwaters in the geological formation is essential because the most likely mechanism for transport of radionuclides from the waste repository is dissolution or suspension in groundwater and migration through the rock matrix and permeable fractures in the bedrock. The chemical composition of the groundwater will affect the stability of the engineered barriers and degradation of the wasteform. The evolution of groundwater system will affect the sorption behavior of the radionuclides that would be released from the disposal system. (Davis and Kent, 1990). Therefore characterisation, interpretation understanding and of groundwater geochemistry form an essential part of performance assessment and safety analysis of radioactive waste repositories.

The major ions constitute a significant part of the total dissolved solids (TDS) present in the groundwater. The concentrations of these ions in groundwater depend on the hydrogeochemical processes that take place in the aquifer system. As the groundwater moves along its path from recharge to discharge, a variety of hydrogeochemical processes alter its chemical composition. Groundwater at the discharge zone tends to have higher mineral composition compared to that at the recharge zone due to the long residence time and prolonged contact with the aquifer matrix (Freeze and Cherry 1979). Owing to the long residence time typical of most rocks considered as host rocks for repository, geochemical equilibrium generally exits between the water and minerals. The study of concentrations of various major ions present in groundwater is used to describe the chemical characteristics of groundwaters and in the identification of geochemical processes. By sampling

It is bounded on the south by the Gulf of Guinea (Fig. 1).

Accra Plains.

Study Area



Fig.1. Location of the Accra Plains

Tele: E-mail addresses: etglover@gmail.com The hydrogeological setting of the Accra Plains is dominated by very old crystalline metamorphic rocks (Dahomeyan gneiss) which belong to the Pan-African terrain also called Dahomeyides (Fig.2)(Attoh, 1998) with the aquifer regimes occurring under water table, semi-confined and confined conditions. The Dahomeyan gneisses are divided into felsic and mafic gneisses and consists of ortho- and para gneisses, schists and migmatities many of which are rich in garnet, hornblende and biotites (Akiti, 1987). The felsic and mafic gneisses, weather respectively to slightly permeable and impermeable calcareous clays.



Fig. 2 Geological map of the Accra Plains

The Dahomeyan gneiss is generally massive and has few fractures. The porosity and permeability of the rocks are very low (0.1-3%). The generally impervious nature of the weathered zone and the massive crystalline structure of the Dahomevan rocks limit their groundwater yielding capacity. Boreholes drilled to depths ranging from 12m to 104m encountered aquifer regimes at a mean depth of 31.6m within a range of 4.6m to 77.0m. The mean thickness of the aquifer was 3.2m and varied from 0.2. to 12.5m. The borehole yield was found to be $1.9m^3/h$. The mean transmissivity was 4.5 m²/d (Darko, 2001).The magnitude of the hydraulic conductivity (K) in the fractured media is 0.2m/day and the storage coefficient of the order 10^{-5} . The specific capacity determined from transmissivity estimate ranged from 0.5 to 21.1 $m^3/dav/m$ with an average value of 5.0m³/day/m. The mean potential yield of the Dahomenyan aquifer was estimated to be $5.9 \text{m}^3/\text{day}$ (Darko et al, 1995).

Other geological units in the Plains include the Togo series, the Accraian series, the Tertiary and Recent sediments. The Togo series occurs mainly to the north western part of the Plains and consist mainly of quartzites and phyllites and occur as outliers in the Plain. They are characterized by many fractures and joints, with an average density of 80 joints per cubic metre. Boreholes drilled to depths ranging from 26.2 m to 91.8 m with a mean depth of 56.2m encountered water bearing bodies at a mean depth of 27.3m. The water bearing zone ranged from 6.0m to 59.0m. The aquifer thickness varies from 0.3m to 14.9 m with a mean value of 3.3m. The yield is also highly variable and ranges from 0.3 to 20.5 m³/hr. The mean transmissivity determined for the confined aquifer is 11.5m²/day with storage coefficient of 10⁻³. The specific coefficient ranges from 1.5 to 127.8 m³/day/m and has a mean value of 31.1 m³/day/m. The mean potential yield was estimated at $174.1 \text{ m}^3/\text{day}$ the highest in the Accra Plain (Darko, 2001).

The Accra Plains lies in the coastal savannah zone and has an equatorial climate characterised by two rainfall seasons of unequal intensities. The period May to July represents the main rainy season with a mean monthly rainfall of over 200 mm. A minor rainy season occurs in September and October with a mean monthly rainfall of about 66 mm. Average annual rainfall is about 800 mm. A dry season occurs from November to April during which period the mean monthly rainfall is about 30 mm per month. The mean monthly temperature ranges from 24.7° C in August to 32° C in March, with an annual average of about 26.8° C. Relative humidity is generally high, varying from 65 % in the mid afternoon to 95 % at night.

Sampling and Analytical method

Groundwater samples from the Accra Plains were collected from existing boreholes in acid washed 250 ml polyethylene bottles. The depth of the boreholes ranged from 40 to 80m. The samples were collected after 10mins of pumping water out of the borehole. The physical parameters (temperature, pH, electrical conductivity and total dissolved solids (TDS)) were measured in the field during sampling using portable field kits. The probes of the portable kits were calibrated in the laboratory on the day of sampling. The samples were tightly capped to protect the samples from atmospheric CO₂ and transported to the laboratory in an ice chest maintained at a temperature of 4 °C. The samples were subsequently filtered in the laboratory with a 0.45μ m pore size filters and stored for in a refrigerator until analysis.

The major cations $(Ca^{2+}, Mg^{2+}, Na^{+} and K^{+})$ were analysed using inductively coupled plasma emission spectrometer (ICP-ES) whilst ion chromatography was used for the anions (HCO_3 , $Cl^{-}, SO_4^{2^-}, NO_3^{-}$) analyses. Aquachem software version 4.0 (Waterloo Hydrogeologic Inc) incorporated with the hydrogeochemical modelling program PHREEQC was used to calculate aqueous speciation and thermodynamic equilibrium conditions of the groundwater samples with respect to the main minerals phases present in the aquifer. The result of the speciation was used to construct mineral stability diagrams with thermodynamic boundary conditions taken from Tardy (1971) to explain the phase transitions occurring in the study area. The Statistical Package for Social Sciences, (SPSS) software version 16 was used to carry out all the statistical analysis. 13 hydrochemical variables (temperature, pH, TDS, electrical conductivity, Ca, Mg, Na, K, HCO₃, Cl, SO₄, NO₃, SiO₂) were used for the analysis. The variables were log-transformed and were vastly dispersed in their distribution. The data were therefore standardized to their corresponding z-scores (Eq. 1) in order to achieve the objectives of normal distribution and homogeneity. $x - \mu$

 $Z = \frac{\pi}{s}$

(1)

where x is the data, μ , s are respectively the mean and standard deviation of the datasets.

Q-mode hierarchical cluster analysis (HCA) was then applied to the standard z-scores of the data. In this study, the Qmode HCA, which groups samples into clusters, was used together with the R-mode HCA which classifies parameters. Squared Euclidean distances were used to classify parameters into initial clusters, whilst the Ward's agglomeration method was used to link the resulting initial clusters. R-mode factor analysis was applied to the standard z-scores of the data to distinguish the contributions of natural processes and anthropogenic inputs to the chemical composition of the groundwater. In the factor analysis, 'principal components' was selected as the solution method, whilst the Varimax rotation was used to maximize the differences among selected factors in order to facilitate interpretation of the results of the analysis.

Results and Discussion

The descriptive statistics of the groundwater samples are summarized in table1.

The groundwater in general was alkaline in nature. Sodium and chloride ions are the dominant ions in the groundwater. The anion chemistry showed that the relative abundance of anions in the groundwater is in the order Cl⁻>HCO₃⁻>SO₄²⁻>NO₃⁻. The chloride concentration constituted about 76% of the total concentration of anions and it ranged from 1.24 to 136.06 meq/L (44 to 4830 mg/L). These values indicate probable seawater intrusion based on values set by Lusczynski and Swarsenski (1996). According to them Cl⁻ concentration of 1.40 meq/L is indicative of seawater intrusion. The HCO₃⁻ concentration varied from 0.31to 14.78 meq/L. Na⁺ ion constitute about 50% of the total cation concentration. The relative abundance of the cations is in the order Na⁺>Mg²⁺>Ca²⁺ > K⁺. The low levels of K⁺ ions in the groundwater can be attributed to its tendency to be fixed by clay minerals and to participate in the formation of secondary minerals (Zhu et al 2006).

The groundwater can be described as brackish as about 56% of the groundwater samples analysed had TDS values greater than 1,000mg/l. According to Freeze and Cherry (1979), brackish water has TDS concentration in the range of 1,000 to 10,000 mg/L. The TDS concentrations have a similar trend as that of the EC. TDS concentrations were relatively low along the foothill of the Akwapim Togo Mountains. This area is probably the recharge area for groundwaters within the Plains (Akiti, 1987) and the groundwaters have short residence time within the rocks which are mainly quartzites with little minerals to be dissolved. The TDS values increase south eastwards through the central part of the Plains towards the coasts. The high saline waters occurring in the central and coastal areas of the Plain suggests that the waters has had enough contact time with the rock minerals and might be saturated with respect to both calcite and dolomite (Kortatsi, 2006).

The Piper (fig.3) and Chadha (fig.4) plots suggest that Na, Mg and Ca and Cl dominate the aquifer. However the groundwater can be distinguished into three water types. Groundwater type 1 is mainly composed of Na-Mg-Ca-Cl-HCO₃. This type of groundwater is found along the foothills of the Akwapim-Togo Mountain where the Dahomeyan and Togo series of rocks underlying the area are known to contain ferromagnesian silicates (hornblende, pyroxenes and biotite). The water type must have evolved from the interaction of the recharging waters with the ferromagnesian silicates. The groundwaters in the area are generally fresh (TDS< 1000mg/l) except for the groundwaters sampled at Presbyterian Women Centre (PWC, Abokobi), Ayikumah (AYK) and Kpong . They had TDS values greater than 1000 mg/L. The groundwater type at PWC was Na-Cl type. The samples from PWC come from quartzites and the borehole is far from the coast. It is therefore doubtful that sea water intrusion could have transversed the gneiss of the Plains. The water facies at Ayikumah and Kpong could be attributed to the presence of marbles in the gneiss at Agomeda (3km from Ayikumah) and the carbonatites at Kpong (Akiti 1980).



Fig.3: Piper trilinear diagram showing hydrochemical facies

Groundwater type 2 is composed mainly of Na-Mg-Ca-Cl and found in most parts of the central area of the Plain. The water is slightly saline or moderately saline as the TDS values range from 1107 to 4495 mg/L. This water type generally characterises mixed water (Akiti 1980).

Groundwater type 3 is found along the coastal zone of the Plain. The waters were composed mainly of Na-Ca-Cl with TDS values ranging from 1760 to 8747 mg/L. The groundwater type is attributed to preferential leaching of high soluble surface or near surface soil NaCl salts, which are completely dissolved during resolution (Akiti, 1980). Subsequent evaporative concentration may also cause the less soluble salts to precipitate out of solution resulting in the percolating water becoming enriched with NaCl (Drever and Smith, 1978).



groundwater The Spearman correlation matrix for the 13 variables is shown in table 2. The resultant matrix shows weak correlation of

shown in table 2. The resultant matrix shows weak correlation of pH with all the variables. It likewise revealed a strong correlation of TDS with EC, Ca, Mg, Na, K, Cl and SO₄ and moderate correlation with HCO_3 and NO_3 . Na, Ca, Mg, SO₄ and Cl have high mutual correlations, indicating that these elements are likely to be combined together.

The R-mode factor analysis resulted in three factors accounting for 83.65% of the total variance in the hydrochemistry of the study area. Table 3 presents the loading of each variable under each of the three factors. The first factor (PC1), which accounts for about 68.94% of the variance, has positive loadings for TDS, EC, Ca²⁺, Mg²⁺, Na⁺, K⁺, HCO₃⁻, Cl⁻, NO_3 and SO_4^2 . The bicarbonate ion (HCO₃⁻) was dropped from the analyses after a series of trials indicated that it loaded highly in more than one factor and was therefore a redundant parameter in the factor analysis. The parameters associated with factor 1 connote salinity enhancement arising from mineral dissolution. It is apparent that rock-water interaction plays a major role in the hydrochemistry. The high positive loading for NO₃ can be attributed to the small scale farming activities that occurs all year through using both surface and groundwater. Animal manure (compost) and chemical fertilizers are being used extensively to increase crop yield. Some of these chemicals infiltrate through recharging waters into the aquifers. The second factor (PC2) accounts for 8.27% of the variance and has positive loading for SiO₂ and HCO₃. The positive loading for SiO₂ could be due to dissolution of the rock mineral feldspars. The relatively high bicarbonate could be the result of reaction of soil CO₂ with alkali-feldspars. The third factor (PC3) accounts for 6.40% of the variance and has a positive loading for pH.

The result of the HCA is illustrated with a dendrogram (fig.5). Three groups and nine subgroups were selected based on

visual examination of the dendrogram each representing a hydrochemical facies.

Group 1 is mainly made up of groundwater samples collected from borehole located along the foothill of the Akwapim Togo range. It makes up about 26.42% of the total groundwater samples. The group is divided into 3 subgroups. The water is relatively fresh with a mean TDS value of 311 mg/L and EC value of 544μ S/cm. The Ca ions had an average concentration of 1.41 meq/L with Mg ion having a mean concentration of 1.56 meq/L. The mean Na ion concentration was 3.11 meq/L. Chloride the dominate anion had a mean concentration of 3.91 meq/L. The low degree of mineralization of these waters suggests that the contact time with rock and soil may have been short.

Group 2 is divided into 5 subgroups and constituent about 54 % of the groundwater. The mean TDS is 1532mg/L with a mean EC value of 2587 μ S/cm. Sodium and chloride are the dominate species in the group. The Ca ions had an average concentration of 5.23 meq/L with Mg ion having a mean concentration of 7.23 meq/L. The mean Na ion concentration was 13 meq/L whilst chloride ion had a mean concentration of 18.61meq/L.

Group 3 had no subgroups and account about 19.58% of the groundwater. The mean TDS is 4985mg/L with a mean EC value of 7783 μ S/cm. The Ca ions had a mean concentration of 16.1 meq/L with Mg ion having a mean concentration of 21.84 meq/L. The mean Na ion concentration was 44.77 meq/L whilst chloride ion had a mean concentrations compared to the other group had very high ion concentrations compared to the other group suggesting a longer contact time with rock and soil. As dissolution of aluminosilicate minerals is a slow process, the increase in TDS and EC from group 1 to group 3 may be interpreted as the consequence of short to long residence time of solutions within the aquifers.



Fig. 5. Dendrogram of HCA containing all the groundwater samples

The evolution of groundwater

Gibb's ratio (Gibbs 1970) for the major cations and anions of the water samples were plotted separately against TDS to understand and differentiate the influences of rock-water interaction, evaporation and precipitation on the water chemistry within the Plains (fig.6 a-b). Most of the groundwater samples plotted in the rock dominance field whilst a few plotted in the evaporation field. This suggests that weathering of the rock forming minerals by the groundwater is one of the major geochemical processes controlling the ion chemistry of the groundwater. The geological formation in the Accra Plains consists of alumino-silicate minerals and weathering of the alumino-silicate minerals particularly plagioclase (albite), hornblende and pyroxenes will contribute to the concentration of Na⁺, Ca²⁺, Mg²⁺, K⁺ and HCO₃⁻ in the groundwater.



Fig 6(a-b). Gibbs plots explain groundwater chemistry and geochemical process in the Accra Plains

The geochemical processes responsible for the evolution of the chemical character of the groundwater were further studied using various chemical ratios in relation to chloride concentration. Chloride concentration was selected as a reference ion following Chereboterev's (1955) hypothesis that the chemical evolution of groundwater along a flow path tends towards the composition of seawater as per the following chemical evolution sequence.

$$HCO_{3}^{-} \rightarrow HCO_{3}^{-} + SO^{2}_{4} \rightarrow SO^{2}_{4} + HCO_{3}^{-} \rightarrow SO^{2}_{4} + CI^{-} \rightarrow CI^{-} + SO^{2}_{4} \rightarrow CI^{-}$$

$$(2)$$

Furthermore, chloride does not enter into precipitationdissolution processes except at brine concentrations and it rarely enters into oxidation-reduction or adsorption reactions (Feth, 1981). Thus chloride can clearly show the evolutionary trends of the chemical character of a groundwater flow system.

Sodium and chloride are the two dominant ions in the groundwater and in many waters they can have the same source. The scatter plot of Na⁺ and Cl⁻ (fig.7) is strongly linear suggesting a mixing trend of more saline water with dilute meteoric water. The samples along the foothill of the Akwapim Togo mountains (group 1) plots along the 1:1 trendline however with increasing ion concentration (group 2 to 3 samples) the ions deviate or plot above the equiline.

The semi-log plot of the same data set (fig.8.) indicates two distinct slopes, a steep slope at low concentrations and a lower slope at high concentrations. The Na/Cl ratio for the steep slope is approximately unity, greater than the sea water ratio of 0.55 (Nordstrom et al 1989). The shallow slope has a ratio of 0.4. The

high ratio is typical of river waters, rainwaters, fresh groundwater and groundwater dominated by halite dissolution. The low ratio tends to occur when other cations, Ca and/or Mg become comparable to or greater than Na in concentration (Nordstrom et al 1989). The bimodal slope suggests a transition from water in the weathered zone at shallow depths and in permeable rocks to water possessing a saline component, enriched in Ca and/Mg and associated with impermeable rocks. Those samples with Na⁺/Cl⁻ ratio value higher than 1 also show a deficit in Ca²⁺ + Mg²⁺. This is consistent with a Ca²⁺–Na⁺ cation exchange process which leads to a softening of the water (Hidalgo and Cruz-Sanjulian 2001). Ca²⁺ and Mg²⁺ can exchange Na⁺ sorbed on the exchangeable sites of the clay minerals, resulting in the decrease of Ca²⁺ and Mg²⁺ and increase of Na⁺ in groundwaters.

The Na⁺/Cl⁻ ratio which ranges from 0.45 to 1.40 generally decreases with salinity indicating that the groundwater is not evolving towards equilibrium (fig.9). Ratios in excess of 1.0 at low salinities imply that meteoric NaCl is not the only source of Na⁺ (Nkotagu, 1996). Albite weathering may be occurring in the bedrock releasing Na⁺, HCO₃⁻ and kaolinite according to the weathering reaction

 $2NaAlSi_{3}O_{8} + 2H_{2}CO_{3} = Al_{2}Si_{2}O_{5}(OH)_{4} + 2Na^{+} + 2HCO_{3} + 4H_{2}SiO_{2}$ (3)





Calcium and magnesium together constitute 48% of the total cations in the groundwater. The pyroxene, amphiboles and calcic feldspars which are common in the mafic rocks will contribute Ca^{2+} and Mg^{2+} in the groundwater as these minerals are easily weathered and add Ca^{2+} and Mg^{2+} to the groundwater system during rainfall infiltration and groundwater movement.

The Mg^{2+}/Ca^{2+} ratio varies from 0.57 to 4.90 over a wide range of salinity with few ratios less than 1 (fig.10). The increase of the ratio with salinity can be attributed to increased cation exchange of Na⁺ with bound Ca²⁺ and Mg²⁺ as salinitiy increases. In addition Ca²⁺ is more electropositive than Mg²⁺ due its lager hydrated size thus keeping the ratio at less than 1. The ratio of Mg²⁺/Ca²⁺ greater than 1 indicates dissolution of amphiboles which results in the addition of more Mg²⁺ ions than Ca²⁺ ions. High Mg²⁺/Ca²⁺ also give an indication of the great age of the groundwater (Akiti 1980).



Fig.8: Semi-log plot of Na⁺ and Cl⁻ concentration



Fig.9. Variation of the Na/Cl with Cl

In the scatter diagram of Ca + Mg vrs HCO_3 (fig.11) most of the samples plot away from the equiline to the 2:1 line indicating predominance of alkali earth by silicate weathering over bicarbonate. Few samples plot in the bicarbonate zone due to the reaction of the feldspar minerals with carbonic acid in the presence of water which releases HCO_3 (Elango et al, 2003).

The $(Mg^{2^+} + Ca^{2^+})/HCO_3^-$ ratio varies between 0.75 and 11.8. The ratio increases with salinity indicating that Ca^{2^+} and Mg^{2^+} are being added to the groundwater at a greater rate than HCO_3 . The high $(Mg^{2^+} + Ca^{2^+})/HCO_3^-$ ratios cannot be attributed to HCO_3 depletion under the existing slightly alkaline geoenvironmental conditions (Nkotagu 1996). Since HCO_3 does not form carbonic acid (H_2CO_3 , (Appelo and Postma, 2005), the excess Ca and Mg might have been contributed to the groundwater from other sources such as reverse ion exchange process (Rajmohan et al 2004). The calcium and magnesium in aquifer material exchanged with sodium in the water as explained by the equation below



Due to the presence of marbles at Agomeda, the carbonatites rocks at Kpong and carbonate rocks identified at GAEC (Kwabenya), carbonate weathering could contribute calcium and magnesium ion to the groundwater. To determine the dominant sources (carbonate or silicate weathering) of the

major ions, Ca+Mg was plotted against Na+K. Most of the samples plotted along the 1:1 trendline (Ca+Mg=Na+K) (fig.12). However few of the samples especially from Group 3 plotted above the 1:1 trendline indicating that although carbonate and silicate weathering contribute ions to the groundwater, silicate weathering dominant the weathering process. Drever (1997) demonstrated that a ratio of $Mg^{2+}/(Mg^{2+} + Ca^{2+})$ in crystalline environment greater than 0.5 indicates silicate weathering. In this study 72.6% of the samples had ratios exceeding 0.5 suggesting that incongruent dissolution of the silicate minerals significantly contribute Mg^{2+} and Ca^{2+} to the groundwater.





The ratio (Na + K)/ total cation (TZ^{+}) is an index used to assess the contribution of cations by silicate weathering. The scatter diagram of Na + K vrs TZ^+ (fig.13) concentration indicates that majority of the samples plot below the equiline but along the Na+ K=0.5TZ⁺ line indicating contribution of cation from silicate weathering according to Datta and Tyagi(1996). This indicates weathering process of both alkali and alkali earth from feldspar along with additional sources like contribution from alkali. saline soil and residence time are major contributing sources for ions in groundwater .This suggests the involvement of silicate weathering in the geochemical processes which contributes mainly sodium and potassium ions to the groundwater. The weathering of soda feldspar (albite) and potash feldspar which are common in the biotite gnesis in the Accra Plains produce kaolinite and contribute Na⁺ and K⁺ ions to the groundwater. Feldspars are more susceptible for weathering and alteration than quartz in silicate rocks.

From the Gibbs plot another dominant process determining the groundwater composition is evaporation. The Accra Plains experiences dry climatic conditions, it is therefore expected that evaporation will influence the groundwater chemistry. it is expected that the evaporation process would cause an increase in concentrations of all the species in the groundwater. If the evaporation process is dominant, assuming that no mineral species are precipitated, the Na/Cl ratio would be constant with increasing electrical conductivity (EC) (Jankowski and Acworth 1997).

The scatter plot of EC vs Na/Cl (fig.14) shows that the Na/Cl ration decreases slightly with increase in EC indicating removal of Na ions by ion exchange. However the Na/Cl ratio remains constant with increasing EC for group 3 groundwater samples. Thus evaporation has influence on the groundwater in the coastal areas of the Plains.



Fig. 14: EC vs Na/Cl scatter diagram

Ion exchange

Ion exchange is one of the important processes responsible for concentration of ions in the groundwater. The existence of abundant Na^+ may promote cation exchange. This can be confirmed by the two indices of base exchange (IBE) namely the chloro alkaline indices (CAI 1 and CAI 2) suggested by Schoeller (1977).

$$CAI \ 1 = Cl - \frac{(Na + K)}{Cl}$$
(5)

$$CAI \ 2 = Cl - \frac{(Na + K)}{SO_4} + HCO_3 + CO_3 + NO_3$$
(6)

(all values expressed in meq/l)

When there is exchange between Na and /or K in groundwater with Mg and/or Ca in the aquifer material both indices are positive indicating reverse ion exchange. If the exchange takes place between Ca and/or Mg in groundwater with Na and/or K in the aquifer material, the indices will be negative, indicating ion exchange. The CAI 1 and CAI 2 values obtained were positive except for a few of the samples in Group 1 which had negative CAI 2 values. This suggests that reverse ion exchange is a dominant process in the groundwater. Calcium and Mg²⁺ exchange Na⁺ sorbed on the exchangeable sites on the aquifer minerals, resulting in the decrease of Ca²⁺ and Mg²⁺ and increase of Na⁺ in groundwaters by reverse ion exchange.

The dominance of reverse ion exchange in the study area was further demonstrated by the Na-Cl and Ca+Mg-HCO₃-SO₄ scatter plot (fig.15). According to Fisher and Mullican (1997) if reverse ion exchange is a geochemical process controlling the composition of groundwater, the relationship between Na-Cl and Ca+Mg-HCO₃-SO₄ should be linear with a gradient of -1. The scattered plot of Na-Cl versus Ca+Mg-HCO₃-SO₄ shows that the points give a straight line (R²=0.94) with a slope of -0.95. This confirms that Ca, Mg and Na concentration are interrelated through reverse ion exchange.



Fig. 15: scattered plot of Na-Cl versus Ca+Mg-HCO₃-SO₄ Thermodynamic Consideration

The computed aqueous speciation was used to define the possible chemical reactions in the aquifer system and to assess the state of equilibrium between the groundwater and minerals. The saturation indices (SI) describe quantitatively the deviation of the groundwater from equilibrium with respect to dissolved minerals. SI is defined as

$$SI = \log^{K_{SP}}$$
 (7)

where *IAP* is the ion activity product of the mineral-water reaction and K_{sp} the thermodynamic equilibrium constant for the mineral at the measured temperature.

About 47% of the groundwater samples were oversaturated with respect to calcite and dolomite (Fig 16). This consists mainly of Group 3 groundwater samples and some of Group 2 samples giving an indication of the long residence time of the groundwater in the aquifer. About 30% of the groundwater samples located along the foothill of the Akwapim Togo mountains (Group 1) were undersaturated with respect to quartz and but all the groundwater samples were undersaturated with respect to amorphous silica. Although quartz is an abundant constitutent of the geologic formation, its slow reactivity does not produce significant variations in the water chemistry (Lasaga 1984) suggesting that the main sources of silica were either amorphous silica or the breakdown of aluminosilicates (Dongarra et al 2009).



Fig.16. Relationship between calcite and dolomite saturation indices

Another approach to test the proposed hydrochemical evolution is the use of mineral stability diagrams (Drever, 1988). Infiltrating water is corrosive and dissolves the aluminosilicate minerals to give argillaceous minerals of which the principal ones are: kaolinite, illite and montmorillonite.

The stability field diagrams of the $Na_2O-SiO_2-Al_2O_3-H_2O$, $CaO-SiO_2-Al_2O_3-H_2O$, $MgO-SiO_2-Al_2O_3-H_2O$ and $K_2O-SiO_2-Al_2O_3-H_2O$ and $K_2O-SiO_2-Al_2O_3-H_2O$ and $K_2O-SiO_2-Al_2O_3-H_2O$.

Al₂O₃-H₂O, (fig.17a-d) systems showed that most of the groundwaters plot essentially in the kaolinite stability field indicating that equilibrium with the kaolinite solid phase is one of the processes controlling groundwater chemistry. Kaolinite is a common weathering product of feldspar and other silicate (Rajmohan and Elango, 2004). However with increasing ionic content and TDS, the groundwaters tends to reach and follow the kaolinite-montmorillonite boundary and eventually to the montmorillonite stability field.

The Na₂O-SiO₂-Al₂O₃-H₂O stability diagram (fig.17c) has much of the data plotting within the Na-montmorillonite field. Na-montorillonite tends to be the stable solid phase in the central and coastal areas of the Plains because of the high concentration of Na⁺ due to the precipitation of calcite, cation exchange and the higher ionic mobility of Na⁺ with respect to Ca²⁺. In terms of the silicate evolutionary sequence these waters are relatively mature. This apparent maturity may be due to the long residence time of the groundwater.

Weathering of primary silicate minerals to kaolinite or gibbsite occurs typically in tropical areas with intense rainfall and under well drained conditions (Appelo and Postma, 2005). However, montmorillonite is most favoured in drier climate where the rate of soil flushing is relatively slow. Thus the Accra Plains with a very dry climate and a mean annual rainfall of 800mm should have most of the groundwater samples plotting in the montmorillonite stability fields. Garrels (1967) demonstrated that initial reactions effected by solutions rich in CO_2 is the production of kaolinite followed by montmorillonite as CO_2 is consumed and the pH, silica and bicarbonate increase in the solution. This thus suggests that the groundwaters which plot in the kaolinite stability field are young or fresh and the groundwater is well drained.







Fig 17a-d: Mineral stability diagrams

Conclusion

The groundwater of the Accra Plains is slightly alkaline and dominated by sodium and chloride ions. The chemical composition of the groundwater is strongly influenced by the rock water interaction, dissolution and deposition of the aluminosilicate rock minerals. Silicate weathering controls the major ion chemistry of calcium, magnesium and sodium and to a lesser extent carbonate dissolution reaction. The ion exchange and reverse ion exchange also controls the chemical composition of the groundwater especially along the coastal areas of the Plain.

The groundwater along the foothill of the Akwapim-Togo mountains are less mineralized than those from the gneiss. The hydrochemical facies evolves from Na-Mg-Ca-Cl-HCO₃ to Na-Ca-Cl following Cherebotarev groundwater flow sequence. The Na-Ca-Cl groundwaters are oversaturated with respect to calcite and dolomite. The long residence time of the groundwater was indicated by saturation of the formation water with respect to some of the solid phases of the rock.

The mineral stability relationship showed that the groundwater generally plots within the kaolinite stability field but evolves towards equilibrium with respect to montmorillonite with increasing cation concentration. This suggests that if one excludes earth-alkaline carbonates, the mineralogical pair kaolinite-montmorillonite would control most of the solution chemistry by direct precipitation.

Knowledge of the variation of groundwater chemistry and its causes is useful in assessing the performance and safety analysis of radioactive waste repositories.

Acknowledgements

This work was carried out with support from the, Training and Research in Italian Laboratory Programme, International Centre for Theoretical Physics and the Institute of Environmental Geology and Geoengineering (IGAG), National Research Council (CNR). Thanks to Dr. Mauro Brilli of IGAG for his assistance in the analyses of the samples. Thanks also to staff of the National Radioactive Waste Management Centre for assisting in carrying out the sampling campaign

Reference

1. Akiti, T. T. (1980). Etudé géochimique et isotopique de quelqués aquifers du Ghana. (Thesis) Univeristé Paris-Sud. 232 pp.

2. Akiti, T. T. (1987). Environmental isotope study of groundwater in crystalline rocks of the Accra Plains, Ghana. Proceedings of the 4th Working Meeting, Isotopes in Nature, Leipzig, September 1986.

3. Appelo C.A.J and Postma, D., (2005) Geochemistry, groundwater and pollution, Balkema, The Netherlands

4. AquaChem software vers. 4.0 (2003) Hydrochemical data analysis, plotting and modelling, Waterloo Hydrogeologic

5. Attoh, K., (1998), High-pressure granulite facies metamorphism in the Pan-African Dahomeyide orogen, West Africa. J. Geol. 106, 236–246.

6. Chadha, D.K. (1999) A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data, Hydrogeology journal, 7 pp 431-439

7. Chapman, N., McCombie, C. (2003): Principles and standards for the disposal of long-lived radioactive wastes. Waste Management Series. Elsevier.

8. Chebotarev, J.I., (1955) Metamorphism of natural waters in the crust of weathering, Geochim. Cosmochim. Acta Vol. 8 pp 137 - 170

9. Darko, P.K., Barnes, E.A., Sekpey, N.K. (1995). Groundwater assessment report on the Accra Plains. Unpublished Technical Report, Water Resources Research Institute (CSIR) Accra

10. Darko, P. K. (2001). Quantitative Aspects of Hard Rock Aquifers: Regional Evaluation of Groundwater Resources in Ghana. Ph.D Thesis, Charles University, Prague, Czech Republic.

11. Datta,P.S., and Tyagi,S.K. (1996), Major ion chemistry of groundwater in Delhi area: Chemical weathering process and groundwater regime. Journal of the Geological Society of India,47,179-188.

12. Davis, J. A. and Kent, D. B. (1990) Mineral-water interface geochemistry. Rev. Mineral. 23, 177–260.

13. Dongarra,G., Manno,E.,Sabatino,G and Varrica,D.(2009) Geochemical characteristics of waters in mimeralised area of Peloritani Mountains (Sicily, Italy), Applied Geochemistry 24,9000-914

14. Drever, J.I. (1988), The Geochemistry of Natural Waters. 2nd edn Prentice Hall, Englewood Cliffs.

15. Drever, J.I. (1997). Weathering Processes. In: Saether, O., and de Caricat, P., editors, Geochemical processes, weathering and groundwater recharge in catchments, Rotterdam, Balkema, Chap. 1 pp 3-19.

16. Drever, J. I. and Smrth. C. L. (1978). Cyclic wetting and drying of the soil zone as an influence on the chemistry of groundwater rn and terrarns. Amencan Journal Science 278, 1448-1454.

17. Elango, L., Kannan, R. & Senthil Kumar. (2003). Major ion chemistry and identification of hydrogeochemical processes of groundwater in a part of Kancheepuram District, Tamil Nadu, India. Journal Environmental Geosciences, 10–4, 157–166.

18. Feth, J.H., (1981), Chloride in natural continental water—A review. U.S. Geol. Survey Water-Supply Paper 2176, 30 pp.

19. Fischer,S.R. and Mullican,W.F. (1997) Hydrogeochemical evolution of sodium-sulphate and sodium-chloride groundwater beneath the northern Chihuahua desert, Trans-Pecos, Texas, U.S.A., Hydrogeology Jornal,5, 4-16

20. Frape, S. K., Fritz, P. and Mcnutt, R. H. (1984) Water-rock interaction and chemistry of groundwaters from the Canadian Shield. Geochem. Cosmochim. Acta 48, 1617–1627.

21. Freeze, A.R. and Cherry, J.A.Q. (1979), Groundwater. Prentice-Hall, Englewood Ciffs, New Jersey 07632.

22. Garrels, R.M., (1967), Genesis of Some GroundWaters from Igneous Rocks. In: Abelson, P.H. (Ed.), Researches in Geochemistry, vol. 2. John Wiley & sons, pp. 405–420.

23. Gibbs, R. J. (1970), Mechanism controlling world water chemistry. Science 170, 1088-1090.

24. Hidalgo, M.C.-L., Cruz-Sanjulian, J., (2001), Groundwater composition, hydrochemical evolution and mass transfer in a regional detrital aquifer Baza basin, southern Spain. Appl. Geochem. 16, 745–758.

25. Jankowski,J. And Acworth,R.I.(1997), Impact of debrisflow deposits on hydrogeochemical process and the development of dry land salinity in the Yass River catchment, New South Wales, Australia, Hydrogeology journal,5,71-88

26. Kortatsi, B.K.,(2006) Hydrochemical characterization of groundwater in the Accra Plains of Ghana, Environ Geol,50, 299-311

27. Lasaga, A.C. (1984), Chemical kinetics of water-rock interactions, J.Geophys. Res. 89, 4009-4029

28. Lusczynski,N.J and Swarzenski W.V.(1996) Saltwater encroachment in Southern Nassau and SE Queens countries, Long Island ,Newyork, US Geol 1613-F

29. Nkotagu, H. (1996) The groundwater geochemistry in a semi-arid, fractured crystalline basement. Area of Dodoma,

Tanzania Journal of African Earth Sciences. Vol. 23, No. 4 pp593-505,

30. Nordstrom, D. K., Andrews, J. N., Carlsson, L., Fonts, J. L., Fritz, P., Moser, H. and Olsson, T. (1985) Hydrogeological and hydrogeochemical investigations on boreholes, Final report of the phase I: geochemical investigations of the Stripa groundwaters. Tech. Rept. 85-06, SKB, 120 pp.

31. Nordstrom, D. K., Ball, J. W., Donahoe, R. J. and Whittemore, D. (1989) Groundwater chemistry and water-rock interaction at Stripa. Geochem. Cosmochim. Acta, 53, 1727–1740.

32. Piper, A. M. (1944) A graphic procedure in the geochemical interpretation of water analyses. Trans. Am. Geophys. Union 25, 914–923.

33. Rajmohan N, and Elango L (2004) Identification and evolution of hydrogeochemical processes in the groundwater environment in a part of Palar and Cheyyar River Basins, southern India. Environ Geol 46:47–61

34. Schoeller, H. (1977). Geochemistry of groundwater.In Groundwater studies-An International guide for research and practice (Ch. 15, pp. 1–18). Paris: UNESCO.

35. SPSS 16.0 (2007) SPSS Inc., Chicago Ill, Raynald Levesque

36. Tardy Y (1971) Characterization of the principal weathering types by the geochemistry of waters from European and African crystalline massifs. Chem Geol 7:253–271

37. Zhu, G.F, Li, Z.Z., Su,Y.H., Ma,J.Z., Zhang,Y.Y.(2007), Hydrogeochemical and isotope evidence of groundwater evolution and recharge in Minqin Basin, Northwest China, J. Hydrology, 33, 239-251

	Minimum	Maximum	Mean	Std. Deviation
Temp °C	24.00	32.10	28.89	1.61
pH	5.60	8.50	7.08	0.53
TDS	50.00	8748.00	1920.00	1893.44
EC (µS/cm)	129.00	13700.00	3130.00	2902.98
Ca	8.00	573.90	133.00	122.92
Mg	6.35	564.87	107.00	105.23
Na	21.00	1892.23	394.00	409.75
K	1.45	70.00	22.81	14.14
HCO3	28.00	595.00	221.00	134.12
Cl	44.00	4830.00	900.00	993.42
SO4	12.86	586.00	145.00	127.57
NO3	0.67	31.00	4.84	4.99
SiO2	3.00	95.45	26.59	19.87
A 11	`			

Table 1: Statistical Summary of geochemical data

(All in mg/L)

	Temp	pН	TDS	EC	Ca	Mg	Na	K	HCO3	Cl	SO4	NO3	SiO2
Temp	1												
pН	0.075	1											
TDS	0.303	0.433	1										
EC	0.285	0.408	0.986	1									
Ca	0.245	0.443	0.920	0.912	1								
Mg	0.252	0.446	0.929	0.912	0.928	1							
Na	0.294	0.399	0.936	0.943	0.883	0.895	1						
Κ	0.306	0.469	0.826	0.825	0.795	0.809	0.809	1					
HCO3	0.107	0.262	0.631	0.616	0.650	0.690	0.557	0.477	1				
Cl	0.299	0.411	0.953	0.950	0.923	0.932	0.970	0.841	0.549	1			
SO4	0.305	0.339	0.802	0.804	0.841	0.837	0.853	0.655	0.585	0.828	1		
NO3	0.227	0.232	0.588	0.599	0.549	0.596	0.606	0.523	0.362	0.611	0.564	1	
SiO2	0.203	0.281	0.196	0.218	0.203	0.296	0.237	0.219	0.335	0.185	0.255	0.228	1

Table 2: Spearman correlation matrix

Table 3: Factor	loadings from the R-mode factor anal	ysis
	Potated Component Matrix	

Rotated Component Matrix							
	PC 1	PC 2	PC 3				
pН	0.261	0.129	0.949				
TDS	0.941	0.121	0.205				
EC	0.945	0.167	0.159				
Ca	0.914	0.161	0.199				
Mg	0.914	0.243	0.194				
Na	0.944	0.123	0.142				
Κ	0.799	0.161	0.21				
HCO ₃	0.593	0.515	0.005				
Cl	0.962	0.077	0.163				
SO_4	0.833	0.231	0.105				
NO ₃	0.623	0.22	0.133				
SiO ₂	0.113	0.938	0.135				