Environ Geol (2006) 50: 299–311
DOI 10.1007/s00254-006-0206-4

ORIGINAL ARTICLE

Benony K. Kortatsi

Hydrochemical characterization of groundwater in the Accra plains of Ghana

Received: 21 January 2003
Accepted: 21 February 2006

B. K. Kortatsi
Water Research Institute, CSIR,
M 32 Accra, Ghana
E-mail: kortatsi@hotmail.com
Fax: +233-21-777170

Abstract Chemical and isotopic analyses are used to characterize and identify the relevant water-rock interactions, which are responsible for the poor groundwater quality in the Accra Plains. Four main water types are identified. Processes that singly or in combination influence the chemical composition of each water type include halite dissolution carbonate dissolution and precipitation, seawater intrusion, cation exchange, evaporative concentration of solutes and aluminosilicates dissolution. These processes contribute considerably to the concentration of major ions in the groundwater. Stable isotope contents of the groundwater suggest mainly direct integrative recharge. A few samples plot along the meteoric-seawater mix line which is coincidentally the evaporative line. The Cl^-/Br^- ratios of some of these are close to 300 confirming marine origin, others probably concentrated by evaporation have their Cl^-/Br^- ratios significantly lower than 300. Groundwater is qualitatively good for drinking purposes only along the foothills of the Akwapim Togoland ranges.

Keywords Accra Plains · Dissolution · Ghana · Groundwater quality · Precipitation

Introduction

Groundwater has become an important source of potable water supply in the Accra Plains due firstly to the fact that the rural communities within the Accra Plains are widely scattered and reaching them with pipe-borne water can be expensive and probably uneconomically. The government of Ghana realising this, has decided to provide boreholes and hand-dug-wells as an alternative to pipe-borne water supply schemes. Secondly, water supply to Accra and Tema municipal areas in the Accra Plains is based on raw water taken from the Volta River and treated at Kpong. This water supply is however, grossly inadequate to meet ever-increasing population and industrial needs. Consequently, major industrial establishments and individuals augment their piped-water supplies with groundwater through the use of boreholes and hand-dug wells.

Accra Plains also provide one of the richest arable lands for large-scale agriculture in the country (Quist 1976; Amuzu 1978). However, due to the scarcity of surface water resources coupled with inadequate and erratic rainfall, full utilization of the agricultural potential of the Accra Plains has not been realized. Nonetheless, small scale or backyard agriculture using low yielding boreholes and hand-dug wells has been on the increase. Thus, the importance of groundwater for drinking purposes, agricultural and industrial purposes in the Accra Plains cannot be over emphasised.

Despite the increasing popularity and usage of groundwater, inadequate yield of boreholes and particularly poor water quality in majority of the boreholes are the limiting factors that hinder further groundwater development in the Accra Plains. Significant number of wells had been abandoned because of quality problems. High salinity and individual chemical parameters appear to be responsible for the poor quality groundwater that is encountered in the Accra Plains (Quist 1976; Amuzu 1978; Akiti 1986; Kortatsi and Jørgensen 2001).

In spite of the quality problems, which apparently are associated with the groundwater, little is known about either the natural processes that govern the chemical composition of the groundwater or the anthropogenic facets that have effect on it. The main objective of this paper is therefore to use existing chemical and isotopic data to characterize the groundwater and to identify the relevant water-rock interactions.

Site description

The Accra Plains lies between longitude 0° 20′ W and 0° 40′ E and latitudes 5° 30′ N and 6° 15′ N respectively and covers approximately 6,000 km^2. It is bounded on the west and the northwest by the Akwapim -Togoland ranges, on the east-northeast by the River Volta and on the south by the Gulf of Guinea. The map of the Accra Plains is presented in Fig. 1.

Geomorphologically, the Accra Plain is generally flat and undulating with a few isolated inselberg that seldomly rise 70 m above mean sea level (Dickson and Benneh 1980). An east–west surface water-divide separates the Accra Plains into two drainage sub-basins. Streams in the northern sub-basin flow eastwards and drain into River Volta while streams in the southern sub-basin flow south and drain into the sea. Apart from the River Volta all other rivers or streams in the Accra Plains are ephemeral.

The climate is characterized by two rainfall maxima. The major rainy season occurs between May and July with the peak occurring in June while the minor one occurs between September and October with the peak occurring in October. Generally, the rainfall in the Accra Plains is low with mean annual value being approximately 900 mm. The mean temperature is 26°C. The vegetation is mainly coastal grassland and scrub (Dickson and Benneh 1980).

Hydrogeological setting

The Accra Plains is largely underlain by the Dahomeyan Formation, which consists of alternating bands of massive acidic and basic gneisses, schists and migmatites

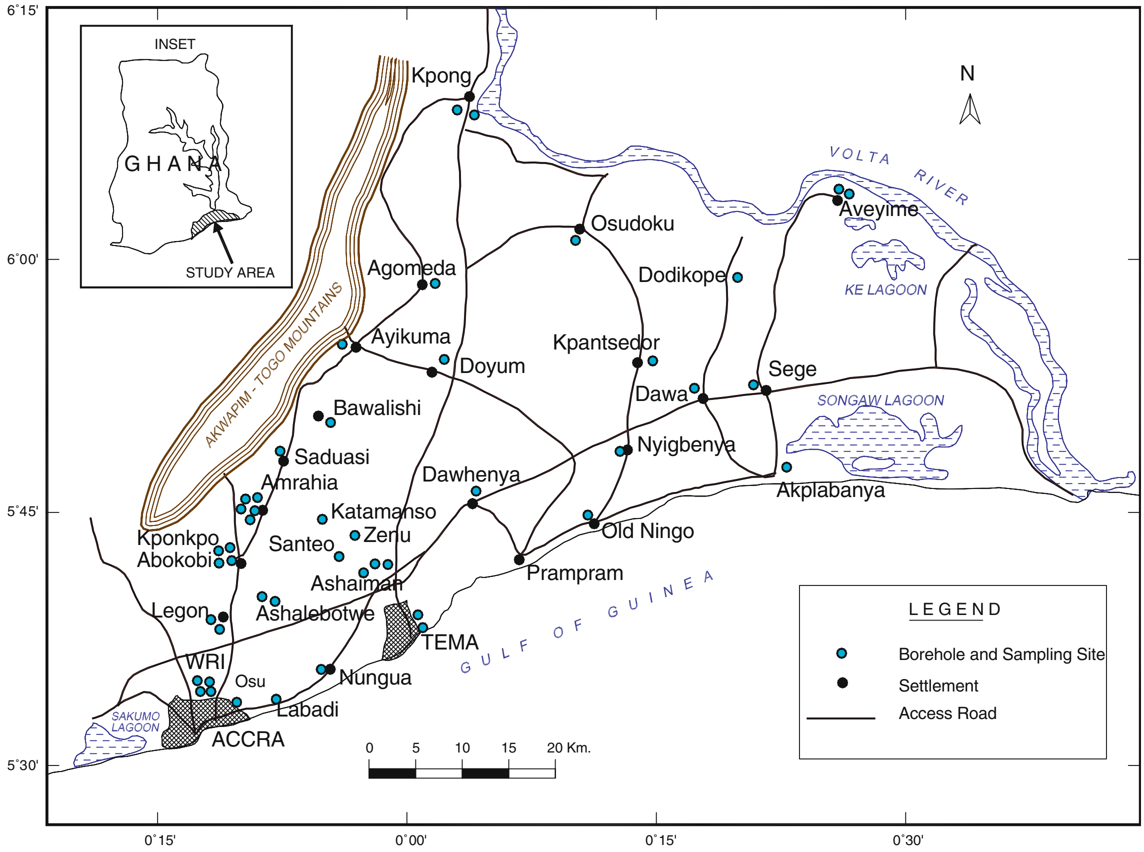


Fig. 1 Location map of the Accra Plains

(Quist 1976; Kesse 1985). Other geological units include the Togo Series, the Accraian Series and the Tertiary and Recent Sediments. The geological map of the Accra Plains is presented in Fig. 2. The Togo Series occurs mainly to the north-western part of the study area and consists mainly of quartzites and phyllites. Other rock types of the Togo Series include sandstones, shales, schists and silicified limestones. The Accraian Series consists of sandstones, grits and shales and are found in the vicinity of the city of Accra. The tertiary and recent sediments occur in the southeastern parts of the study area close to the estuary of the River Volta (Fig. 2).

Groundwater occurrence in the Accra Plains is controlled mainly by the development of secondary porosity, e.g., fractures, faults, joints and the associated weathered zones since the rocks are inherently impermeable. The acidic rock types weather to slightly permeable calcareous clay whereas the basic rocks weather to impermeable clay (Junner and Bates 1945). The quartzites and phyllites of the Togo Series weather to sandy clay. The depth of the weathering is highly variable and it is greatest along the foothills of the Akwapim – Togo ranges where it has reached 47 m and least in the heart of the Accra Plain where it rarely exceeds 6 m (Quist 1976). Aquifers, as in the case of most crystalline formations, occur either in the weathered zone, the transition zone between the weathered and the fresh rock or in the fractured zone. The weathered zone aquifers generally occur at the average depth of 25 m and are either semi-confined or phreatic. The fractured aquifers generally occur between the depths of 35 m and 65 m and are mainly semi-confined or confined. The aquifers are generally discontinuous. Principally, recharge to the aquifers is by direct percolation of rainfall along the foothills of the Akwapim-Togoland ranges (Akiti 1980). Minor or indirect recharge also occurs mainly in the rainy season when fractures or mega joints intercept the ephemeral stream course. These channels act as conduits that allow water to recharge the aquifer. Recharge of the groundwater system is estimated as 15% of the annual precipitation (Nii Consult 1998).

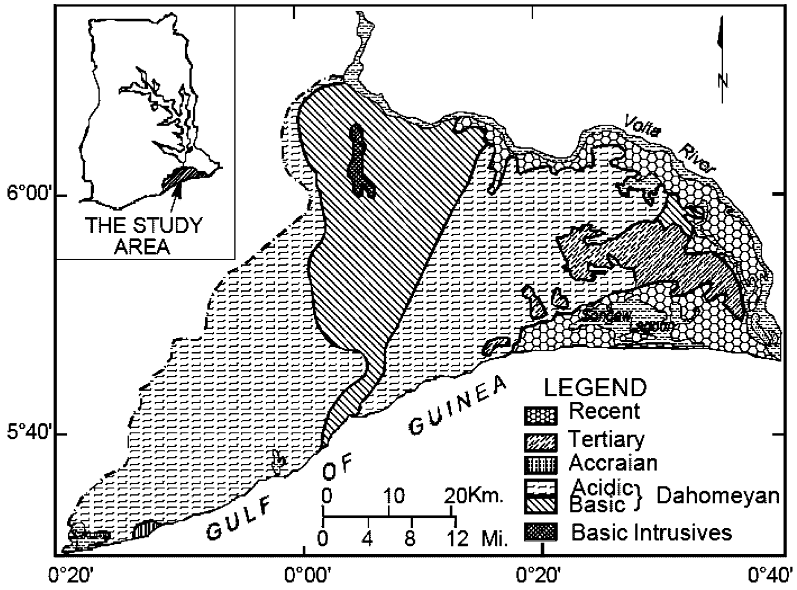
Borehole yields for standard size well (125 mm diameter) with median depth of 52 m are in the range 0.7–27.5 m^3 h^{-1} with a mean value of 2.7 m^3 h^{-1}. Transmissivity values are generally low due to the clayey content of the regolith. They vary from 0.2 m^2 h^{-1} in the clayey regolith to 4.0 m^2 h^{-1} in the fissured zones (WRRI 1996).

Methodology

Water samples for physico-chemical analysis were collected from 164 boreholes in the Accra Plains in November 2000. Two samples were collected at each site using laboratory cleaned high density linear polyethylene (HPDE) 100 ml bottles. Sampling protocols described by Claasen (1982) and Barcelona et al. (1985) were strictly adhered to. Samples for cation analysis were filtered using a sartorius polycarbonate filtering apparatus and a 0.45 μm cellulose acetate filter membrane samples and acidified with Merck ultra pure nitric acid to a pH <2 in the field. Samples for anion analyses were without preservation. Unfiltered groundwater samples were collected in 30-ml glass bottles with poly-sealed lids for stable isotopic analyses.

Temperature, redox potential (Eh), pH and electrical conductivity (EC) measurements were conducted on-site

Fig. 2 Geological map of the Accra Plains



using WTW-Multiline P4 Universal Meter in an anaerobic flow-through cell attached in line to borehole pump outlet. Prior to these analyses, clear pumping was carried out until stable meter readings of these parameters (pH, Eh and EC) were obtained. This was done in order to avoid the sampling of stagnant annulus water that would be in the region of pump and pump systems. The mean time for clear pumping was 10 min. Alkalinity titration was done at the wellhead using HACH Digital Titrator Model 16900. All major ions sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{2-}) as well as some trace elements such as nitrate (NO_3^-) and fluoride (F^-) were analysed using double column Dionex DX-500 ion chromatograph at the Ecological Laboratory, University of Ghana. Stable isotope (deuterium and oxygen-18) analyses were carried out at the University of Copenhagen.

Results and discussions

Summary statistic

Statistical summary of hydrochemical parameters measured in the groundwaters of the Accra Plains is presented in Table 1. The major ions are plotted in frequency versus percentage milliequivalent of the total cations or anions as in Fig. 3. Sen and Al-Dakheel (1986) defined the relative content of a cation or anion as the percentage of the milli-equivalent per litre (meq l^{-1}) of the total cations or total anions, respectively. Pie diagram of median concentrations of major cations and anions in milli-equivalent are plotted in Fig. 4 since median values are much more robust descriptors of non-normal distributions than mean values. Perusal of Table 1 indicates that the groundwater is generally moderately saline or brackish. Brackish water has the total dissolved solids concentration in the range 1,000–10,000 mg l^{-1} (Davis and DeWiest 1966; Freeze and Cherry 1979). Indeed, approximately 75% of the boreholes show TDS levels higher than 1,000 mg l^{-1}. Figure 3 shows that Na^+ and Cl^- are the dominant cation and anion, respectively. These are the only ions that exceeded the 50% of total cations or anions in most boreholes. A further illustration of this is shown in Fig. 4 where the median values of both Na^+ and Cl^- exceeded 50% of total cations and anions in milli-equivalent unit, respectively. Figure 4 also shows that the order of relative abundance of major cations in the groundwater of the Accra Plains is $Na^+ > Mg^{2+} > Ca^{2+}$ while that of anions is $Cl^- > HCO_3^- > SO_4^{2-}$. Since most of the chemical parameters were not normally distributed, correlations between major ions were carried out using Spearman's correlation analysis. The results are shown in Table 2. High positive correlation ($r = 0.84$) was found between Na^+ and Cl^- and very high positive correlation ($r = 0.90$) between total dissolved solids (TDS) and both Na^+ and Cl^-. The correlations between TDS and Mg^{2+} ($r = 0.64$) and $SO4^{2-}$ ($r = 0.58$) are low but also significant ($r = 0.3$) at 1% level. On the other hand, correlations between other ions and TDS and among themselves though positive($r < 6.0$ at 1% level) are significantly low suggesting that TDS is derived mainly from Na^+ and Cl^-. Since the correlation coefficient between Na^+ and Cl^- is positively high, it can also be deduced that for most of the groundwater samples Na^+ and Cl^- originate from a common source.

Groundwater temperatures vary from 25.6° to 31.0°C with median, mean and standard deviation values of 30°, 29.6° and 2.2°C, respectively. The small range of values shows the uniformity of groundwater temperatures within the Accra Plains. The pH values are in the range 5.6–8.1 with a mean value of 7.20 and median and standard deviation of 7.2 and 0.5 respectively indicating that the waters are generally neutral to slightly alkaline. There is, however, no clear spatial distribution pattern. Groundwater conductivity values vary from 222 µS/cm in the north-northwest along the foot-hills of the Akwapim-Togoland ranges to 22,500 µS/cm along the coast (Fig. 5).

Table 1 Summary statistic of chemical parameters in groundwater samples from the Accra plains

Parameter	Minimum	Maximum	Median	Mean	SD	95% Confidence interval
Ca^{2+}	4	2090	72	72	4.4	56–88
Mg^{2+}	2	724	48	46	4.8	31–53
Na^+	20	5370	291	291	3.1	245–345
K^+	1	302	22	20	2.7	19–25
HCO_3^-	5	1136	187	158	4.1	120–196
SO_4^{2-}	6	1023	124	113	2.7	95–133
Cl^-	58	8511	581	568	3.1	478–674
SiO_2	0.1	65	39	38	3.8	36–40
TDS	110	14454	1742	1695	2.3	1491–1927
pH	5.6	8.1	7.2	7.2	0.5	7.0–7.7
T (°C)	25.6	31.0	30.0	29.6	2.2	28.1–30.2

Concentration values in mg l^{-1}

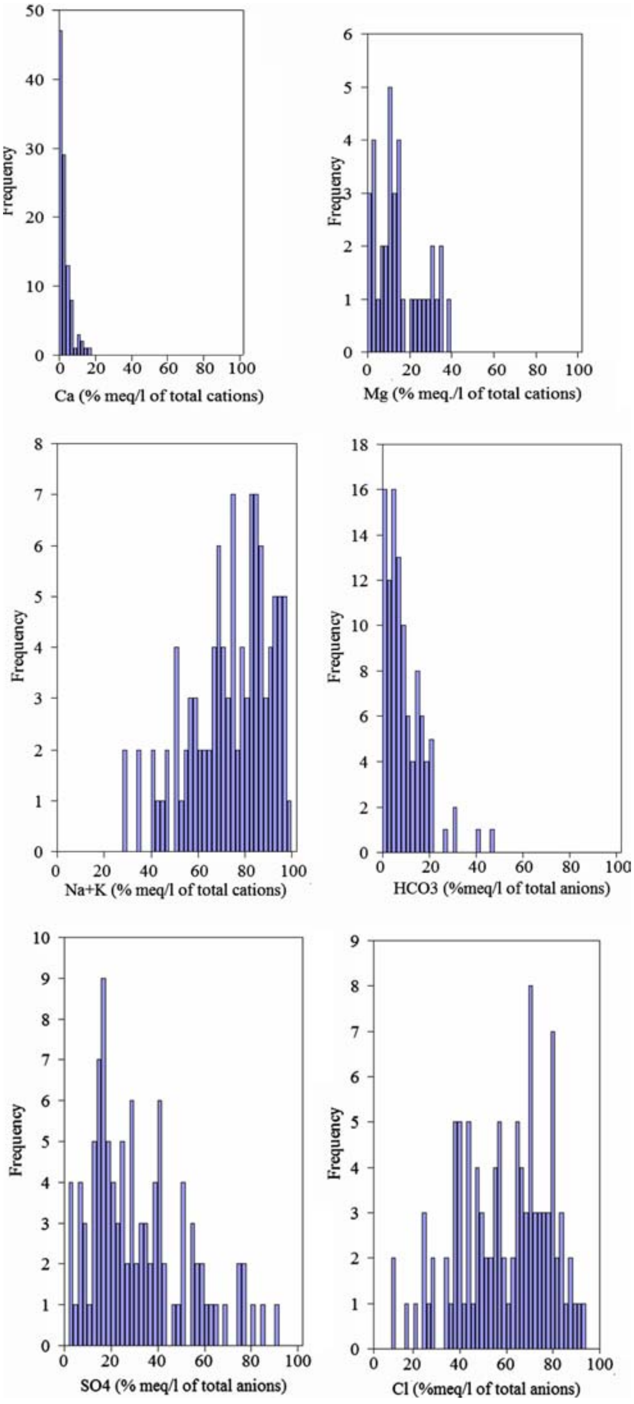


Fig. 3 Percentage frequency distribution of major ions concentration

Water types

Groundwater in the Accra Plains can be broadly divided into four water types. These are illustrated in the expanded Durov diagram of representative groundwater samples in Fig. 6 (Durov 1948; Lloyd and Heathcote 1985). Water type 1 is mainly Na-Mg–HCO_3 type and this composition probably evolved from the interaction of recharging waters with ferromagnesian silicates or reverse cation exchange (Lloyd 1965). This water type occurs mainly close to the foot-hills of the Akwapim-Togoland ranges in the north-northwest of the Accra Plains (Fig. 1) where the Dahomeyan and the Togo Series rocks, as well as the basic intrusives that underlie the area, are known to contain ferromagnesian silicates particularly hornblendes, pyroxenes and biotite (Kesse 1985). Reverse cation exchange could occur as a result of fresh water recharge from the Akwapim-Togoland Ranges flushing out the relatively higher TDS waters of the Accra Plains. In this case, Ca^{2+} is favored by natural ion exchange mechanism than Mg^{2+} and Na^+ and thus removed from solution (Appelo and Postma 1999). The probable exchange reaction for the removal of calcium from the groundwater is given in equation (1)

$$(Ca^{2+} + Mg^{2+}) - 4(HCO_3^-) + 2(NaX) \\ = CaX_2 + Mg - (HCO_3)_2 + 2Na - HCO_3 \qquad (1)$$

where X is the soil exchanger.

The second water type is the Na-Cl water type. This is the dominant water type and will be shown later that it apparently evolves from a combination of processes that include halite dissolution from the soil zone, seawater intrusion and evaporative concentration. This water type occurs in most part of the plain but mainly along the coast and in the middle of the plain. The third water type, the magnesium chloride (Mg-Cl_2) and/or calcium chloride (Ca-Cl_2), occur mainly in the heart of the plains and also close to the coast. This water type probably evolved from seawater intrusion followed by cation exchange as in Eq. (2) (Appelo and Postma 1999).

$$2NaCl + MgX_2 = 2NaX + MgCl_2 \qquad (2)$$

where X signifies the exchanger.

The fourth water type is the mixed water. In this water type, neither a particular cation nor anion is dominant. This water type plots in the middle of the diagram.

Spatial distribution of salinity and hydrochemical zones

Figure 5 illustrates the spatial distribution of TDS in the groundwater of the Accra Plains. Due to the discrete/discontinuous nature of aquifers, contours have not been used for this illustration. TDS levels are relatively low, generally below 1,250 mg l^{-1}, along the foothills of the Akwapim-Togoland ranges. It increases south-eastwards through the centre of the plains toward the coast where TDS values as high as 14.454 mg l^{-1} are

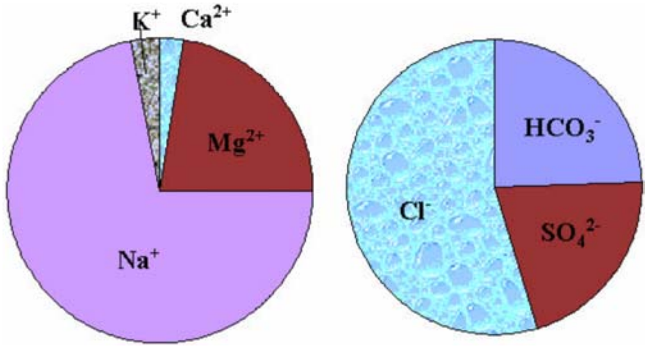


Fig. 4 Pie diagram of median values of major ions

encountered. Generally, therefore, the Accra Plains can be divided into three main hydrochemical zones according to TDS values. These are the Foothill Zone, the Central Zone and the Coastal Zone. The Foothill Zone consists of low salinity groundwater with TDS values rarely exceeding 1,500 mg l^{-1}. The water is mainly water type 1 or Na-Mg-HCO_3 water. The Coastal Zone has high salinity groundwater with TDS ranging between 5,000 and 14,454 mg l^{-1}. The main water types in the Coastal Zone are Na-Cl and Mg-Cl in character. The TDS level of groundwater in the central zone is intermediate between the Foothill Zone and the Coastal zone (1,500–5,000 mg l^{-1}).

Saturation indices, carbonate dissolution/precipitation

The state of saturation of the groundwater with respect to important carbonate mineral (calcite and dolomite) was determined using the hydro-geochemical model Phreeqc for Windows (Parkhusrt and Appelo 1999). This determination was done in order to investigate the thermodynamic controls on the composition of the water and also to calculate approximately the level to which the groundwater has equilibrated with these carbonate phases within the rock matrix. The saturation index (SI) of a given mineral is defined in Eq. (3) as:

$$SI = \log_{10} \quad (IAP/K_{sp}) \qquad (3)$$

Where IAP is the ion activity product and K_{sp} is the solubility product at a given temperature (i.e., the thermodynamic equilibrium constant adjusted to the temperature of the given sample). The thermodynamic data used in this computation are those contained in the database of the *Phreeqc for Windows software*.

Table 2 Spearman rank correlation coefficients of major ions concentration in the groundwater of the Accra plains

	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	TDS
Mg^{2+}	0.31							
Na^+	0.38	0.54						
K^+	0.02	0.10	0.08					
HCO_3^-	0.26	0.39	0.41	0.19				
SO_4^{2-}	0.22	0.25	0.37	0.00	0.08			
Cl^-	0.56	0.63	0.84	0.03	0.39	0.35		
TDS	0.49	0.64	0.90	0.09	0.45	0.58	0.90	
SiO_2	0.05	0.22	0.15	0.24	0.19	0.02	0.16	0.16

r = 0.3 significant at 1% level

An index (SI), less than zero, indicates that the groundwater is undersaturated with respect to that particular mineral. Such a value could reflect the character of water from a formation with insufficient amount of the mineral for solution or short residence time. An index (SI), greater than zero, specifies that the groundwater being supersaturated with respect to the particular mineral phase and therefore incapable of dissolving more of the mineral. Such an index value reflects groundwater discharging from an aquifer containing ample amount of the mineral with sufficient resident time to reach equilibrium. Nonetheless, super saturation can also be produced by other factors that include incongruent dissolution, common ion effect, evaporation, rapid increase in temperature and CO_2 exsolution (Langmuir 1997). Computed saturation indices for calcite and dolomite based on the analysed chemical results and measured field temperatures of the groundwater are plotted in Fig. 7. Such a plot is extremely important in that it gives valuable information on the two most prolific minerals that provide the bulk alkalinity (Nielsen and Grammeltvedt 1993).

In Fig. 7, dolomite saturation is indicated on the x-axis and the calcite saturation on the y-axis. A central band of 0.4 units wide along each axis represents essential equilibrium with respect to calcite and dolomite to account not only for the possible errors that may have occurred in the measurement of pH but also in the measurement of Mg^{2+} and Ca^{2+} (Langmuir 1971). The four quadrants of the plotting field outside the equilibrium area lettered A to D represent different kinds of non-equilibrium conditions with respect to both carbonate species. Quadrant A represents super-saturation with respect both dolomite and calcite. This super-saturation condition probably arises when water that is brought to equilibrium with these carbonate species is subsequently transported into a different environment where a higher pH is attained due to loss of CO_2 or other means. The condition may also arise due to the failure of the measured pH to accurately represent the actual equilibrium pH of the water in the aquifer (Langmuir 1971). Samples falling into this quadrant will precipitate calcite or dolomite. Most of the groundwater samples that plot in this field are those from the central and the coastal zone. Quadrant B represents super saturation

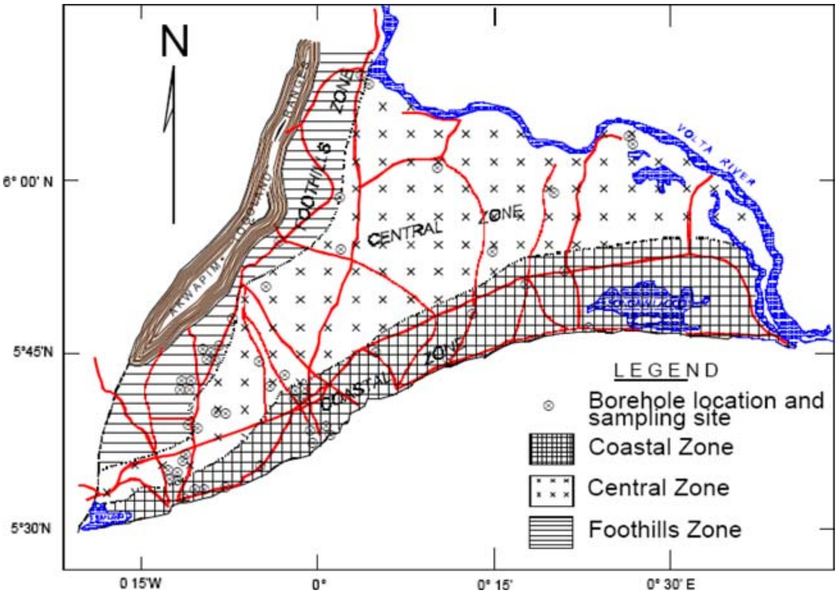


Fig. 5 Groundwater zones according to spatial distribution of TDS (mg l^{-1})

with respect to calcite but under saturation with respect to dolomite. Analyses plotting in this field represent water that is undergoing incongruent dissolution of dolomite and/or precipitation of calcite. Samples that plot here are mainly samples from the central portion of the Accra Plains.

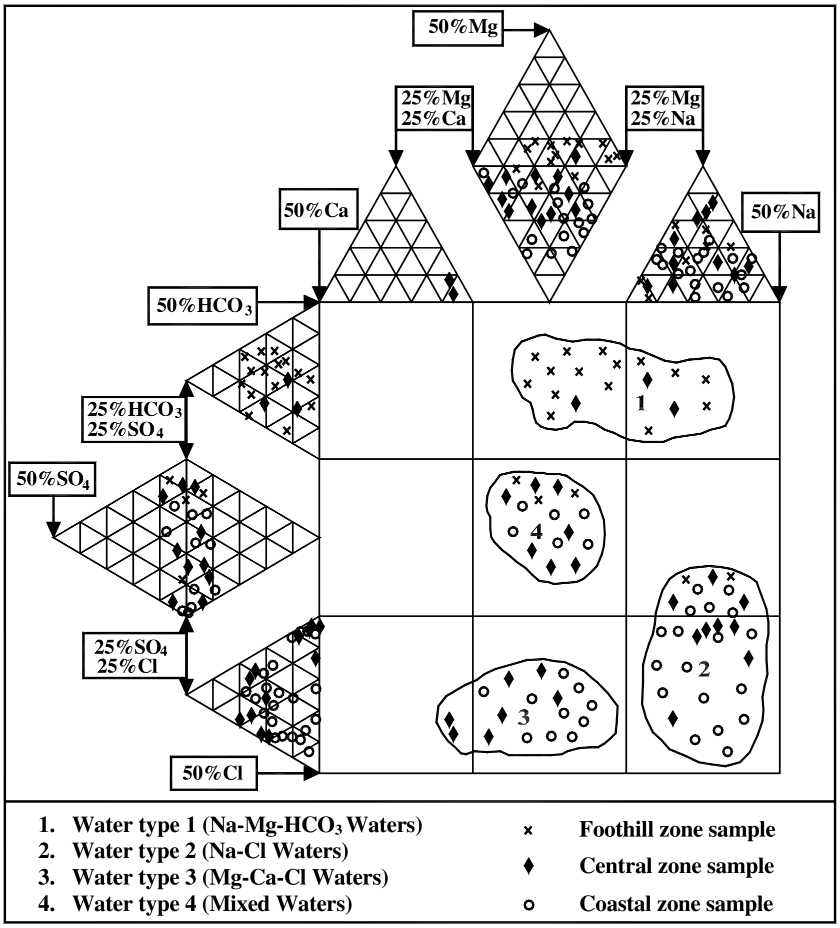
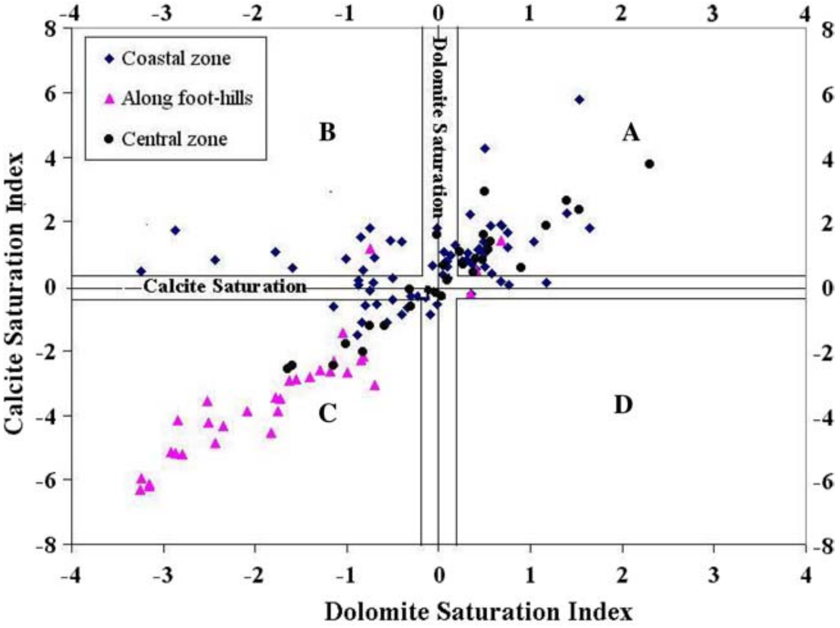


Fig. 6 Expanded Durov diagram of major ions

Fig. 7 Relationship between calcite and dolomite saturation indices



Quadrant C represents under-saturation with respect to both calcite and dolomite. An analysis plotting in this quadrant probably represents water that has come from an environment where calcite and dolomite are impoverished or where Ca^{2+} and Mg^{2+} exist in other forms. Water that has not reached equilibrium with the carbonates because of short residence time would also probably plot in this quadrant (Langmuir 1971). Waters of this type will dissolve calcite if the water comes into contact with a calcite or dolomite source. Samples from boreholes along the foothills of the Akwapim-Togoland ranges mainly plotted in this field. Quadrant D represents super-saturation with respect to dolomite and undersaturation with respect to calcite. None of the water samples plot in this field.

Halite dissolution

Chloride/total anion ratios ($Cl^-/\sum$anions) for approximately 65% of the 160 groundwater samples are greater than 0.8 suggesting that the groundwater possibly originates from halite dissolution, seawater intrusion, brine or evaporites. Groundwater derived from halite dissolution would have $Na^+/(Na^+ + Cl^-)$ ratio of approximately equal to 0.5 (Hounslow 1995). That is $Na^+ \approx Cl^-$. Nearly 60% of the boreholes with $Cl^-/\sum$anions anions ratio greater than 0.8 also have $Na^+/(Na^+ + Cl^-)$ of approximately 0.5 or plot along the 1:1 line in Na-Cl diagram as shown in Fig. 8. This suggests that roughly 60% the boreholes within the Accra Plains derive their salinity mainly from the dissolution of halite. This assertion is consistent with the study of Brammer (1967) who observed high halite content in the soils in part of the Accra Plains.

Seawater intrusion and ion exchange

The remaining borehole samples that have $Cl^-/\sum$anions ratio greater than 0.8 also have $Na^+/(Na^+ + Cl^-)$ ratio

Fig. 8 Plot of Na versus Cl

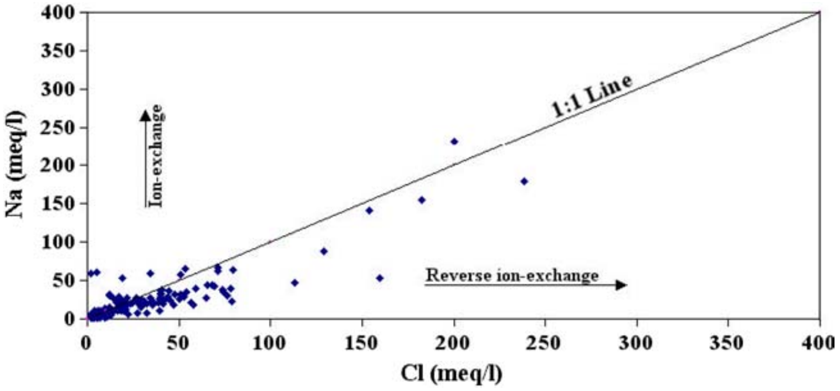


Table 3 Ratios of chemical parameters of representative groundwater samples

Samples	Location	Mg/Ca	Ca/Na	Cl/Br	Na/(Na + Cl)	Cl/SO$_4$	Cl/∑anions (meq ratio)
1	Legon (UG)	2.4	0.11	165.3	0.5	64.6	0.8
2	Akpoman	3.9	0.04	–	0.5	19.9	0.9
3	Abokobi	2.2	0.13	181.1	0.5	7.4	0.8
4	Abokobi Presby	2.5	0.02	51.1	0.5	190.3	1.0
5	Oyarifa	1.5	0.33	–	0.4	4.2	0.7
6	Ayimensah	76.6	0.00	127.2	0.5	6.2	0.7
7	Damfa (N/w) B/H	2.4	0.35	290.9	0.4	43.0	0.7
8	Damfa (S/E0B/H)	2.2	0.28	70.0	0.4	42.1	0.7
9	Damfa (HDW)	1.0	0.18	42.1	0.6	5.7	0.4
10	AShaima[a]	1.8	0.20	339.2	0.4	13.2	0.9
11	Trade fair site[a]	7.0	0.06	307.6	0.4	21.1	0.9
12	TTL(AP170)[a]	2.5	0.20	304.7	0.4	13.0	0.8
13	TTL (AP175)[a]	59.6	0.10	345.9	0.4	14.5	0.9
14	Tema[a]	2.7	0.31	295.7	0.4	17.8	0.8
15	Tema (AP174)[a]	6.1	0.04	317.1	0.4	98.9	1.0
16	Legon (Presec.)	0.9	1.21	8.6	0.3	7.6	0.6
17	Fafraha	1.4	0.25	135.2	0.4	9.5	0.7

[a]Coastal samples i.e. borehole sampled within the 15 kms of coastline

of less than 0.5 suggesting that they are either derived from seawater intrusion or brine (Hounslow 1995). In order to ascertain plausibility of the groundwaters being derived from marine origin, chloride (Cl^-) to bromide (Cl^-/Br^-) ratios of some of the groundwater samples were measured. Cl^-/Br^- ratio (both anions in mg l^{-1}) close to 300 gives a signature of marine component (Mazor 1976). Table 3 shows the Cl^-/Br^- ratios of some of the groundwater samples taken from boreholes in the Accra Plains. Samples close to the coast (< 15 km) have their Cl^-/Br^- ratio values in the range 304–345.5 suggesting marine input or a degree of seawater intrusion. Further evidence of seawater intrusion is provided by the existence of $CaCl_2$ or $MgCl_2$ waters in some boreholes a few kilometres from the coast. According to Appelo and Postma (1999) when seawater intrudes into fresh coastal aquifer $CaCl_2$ or $MgCl_2$ waters results. In this case, Na^+ of the seawater is being replaced with either Ca^{2+} or Mg^{2+} of the clay minerals whereby Na^+ is being adsorbed onto the clay mineral surface. Another evidence of ion exchange is provided by the $Ca + Mg–SO_4–HCO_3$ versus Na-Cl diagram. Water undergoing ion exchange would plot along a line with a gradient of −1 on $Ca + Mg–SO_4–HCO_3$ versus Na-Cl diagram (Jankowski et al. 1998). The groundwater samples from the Accra Plains with $Cl^-/\sum$anions ratios greater than 0.8 but lower $Na^+/(Na^+ + Cl^-)$ ratios than 0.5 are plotted on bivariate plots of $Ca + Mg–SO_4–HCO_3$ versus Na-Cl diagram as can be seen from Fig. 9. The samples plot along a line with a slope of −0.96 which is approximately equal to one indicating that ion exchange is indeed taking place and thus strengthening the evidence of the existence of ion exchange and therefore the intrusion of sea water into the groundwater of the Accra Plains. A consequence of ion exchange is also the super saturation of the groundwater with respect to calcite and dolomite in most of the boreholes from the coastal and the central part of the Accra Plain where $CaCl_2$ or $MgCl_2$ waters are found.

Weathering of silicate

The groundwater data from the Accra Plains suggest that weathering of alumino-silicates particularly plagioclase (albite), hornblende and pyroxenes partially contribute to the concentrations of Na^+, Ca^{2+}, Mg^{2+}, HCO_3^- and H_4SiO_4. These alumino-silicates minerals are present in the rocks of the Dahomeyan and also in the sandstones of the Togo Series outliers. The reaction involving the incongruent dissolution of plagioclase (albite) to kaolinite, montmorillonite and/or gibbsite can be represented by Eqs. (4), (5) and (6), respectively.

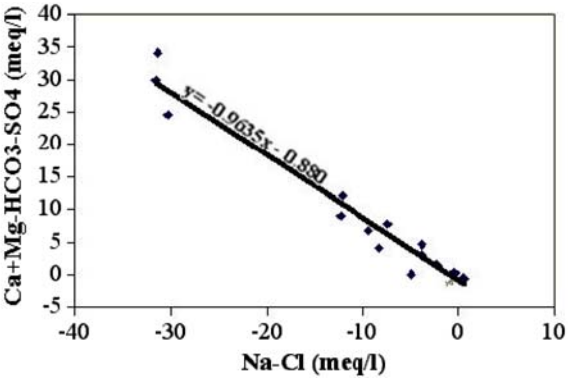


Fig. 9 Bivariate plots of Ca^+ $Mg^-SO_4^-$ HCO_3 versus Na-Cl

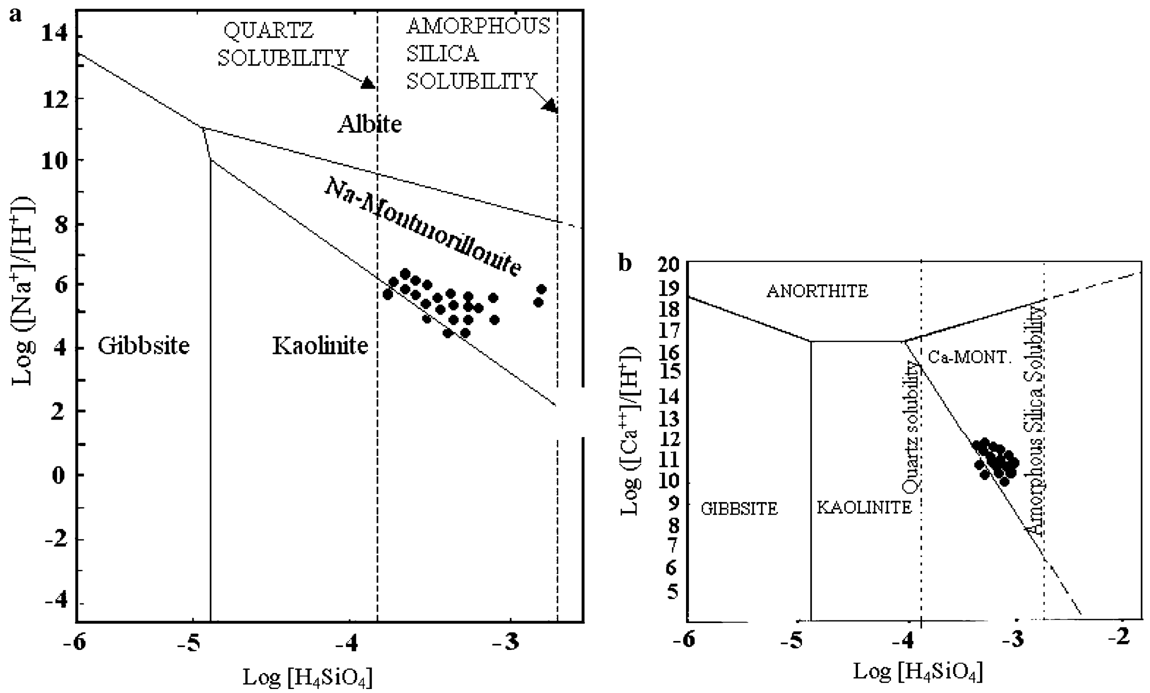


Fig. 10 **a** Stability of Na-Al-Silicate system relative to groundwater from the Accra Plains. **b** Stability of Ca-Al-Silicate system relative to the groundwater from the Accra Plains. Phase boundaries are plotted using thermodynamic data of Tardy (1971)

$$\underset{\text{Albite}}{2NaAlSi_3O_8} + 2CO_2 + 11H_2O = \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 2Na^+ + 2HCO_3^- + 4H_4SiO_4 \quad (4)$$

$$\underset{\text{Albite}}{2NaAlSi_3O_8} + Mg^{2+} + 4H_2O = \underset{\text{montmorillonite}}{2Na_{0.5}Al_{1.5}Mg_{0.5}Si_4O_{10}(OH)_2} + 2Na^+ + H_4SiO_4 \quad (5)$$

In Eq. (5), the presence of Mg^{2+} could be assumed to be leached from chlorite $[MgFe_5Al(AlSi_3)O_{10}]$ or biotite $[K(Mg,Fe)_3AlSi_3O_{10}(OH)_2]$ or pyroxenes $[(Mg,Fe)_2SiO_4]$ which are contained in the gneisses of the Dahomeyan rocks.

$$\underset{\text{Albite}}{NaAlSi_3O_8} + CO_2 + 8H_2O = \underset{\text{gibbsite}}{Al(OH)_3} + Na^+ + HCO_3^- + 3H_4SiO_4 \quad (6)$$

The H_4SiO_4/Na^+ molar ratios according to the stoichiometry of the dissolution of albite to kaolinite, montmorillonite and gibbsite are 2.0, 0.5 and 3.0, respectively. H_4SiO_4/Na^+ molar ratios for the groundwater in the Accra Plains range from 0.06 to 2.8 with mean values of 0.1. These values do not clearly show an indication that albite weathering to clay mineral (kaolinite, montmorillonite or gibbsite) has occurred in the Accra Plains. However, stability diagrams of albite and anorthite with respect to their respective possible weathering products gibbsite, kaolinite and Na or Ca montmorillonite indicate that the groundwaters are in equilibrium with Na and Ca montmorillonite. Figures 10a and b are drawn assuming end member compositions utilizing the equilibrium relationship of Tardy (1971) for standard temperature and pressure (25°C and 1 atm). Log ($[Na^+]/[H^+]$), Log($[Ca^{2+}]/[H^+]^2$) and Log $[H_4SiO_4]$ where [ ] symbolizes activity were computed using Phreeqc for Windows Software (Parkhusrt and Appelo 1999). The type of weathering product obtained depends on hydrological conditions and also the rate of mineral weathering (Appelo and Postma 1999; Brady 1974; Brady and Walther 1989). Weathering of primary silicate minerals to kaolinite or gibbsite occurs typically in tropical areas with intense rainfall and under well drained conditions. Conversely, montmorillonite is mostly favored in drier climate where the rate of soils flushing is relatively slow (Appelo and Postma 1999). Thus the plotting of the groundwaters in Ca-montmorillonite stability field in Ca-Al silicate phases diagram and in Na- montmorillonite stability field in Na-Al-silicate phases diagram during the incongruent dissolution of Ca-feldspar (anorthite) and/or Na-feldspar (albite) are very consistent with hydrological conditions in the Accra Plains. Accra Plains is the driest part of Ghana with average annual rainfall figure of approximately 800 mm per year. Thus, in spite of the lower H_4SiO_4/Na^+ molar ratios than the ratio that is consistent with the stoichiometry of silicate weathering, aluminosilicates weathering is actively taking place. Processes such as ion exchange, halite dissolution as well as saline water intrusion have contributed greatly to the Na^+ concentrations in the groundwater thus lowering the H_4SiO_4/Na^+ molar ratios and as such masking the effect of aluminosilicates weathering.

Stable isotopes

The results of the stable isotope (deuterium and oxygen 18) analyses of 17(No) representative groundwater samples indicate that δ^{18} O varies from $-3.88‰$ to $-2.09‰$ with mean and median values of -3.01 and $-3.18‰$, respectively. The δ^2H values vary from -20.8 to $-8.9‰$ with mean and median values of -14.05 and $-14.2‰$, respectively. The plot of δ^2H versus δ^{18} O is presented in Fig. 11. Most of the groundwater samples plot along the global meteoric water line (GMWL) defined as $\delta^2H = 8\ \delta^{18}O + 10$ (Craig 1961). However, a few of the samples plot along the seawater-meteoric water mix line (SW-MWM) that has the regression equation of $\delta^2H = 4.9\delta^{18}O + 0.6$. Incidentally, this line also coincides with the evaporative water line suggesting that either these samples belong to groundwater that had undergone evaporation on the surface before recharge or had a component of seawater intrusion. Figure 12 is a plot of EC against $\delta^{18}O‰$. It illustrates a good correlation between EC and $\delta^{18}O‰$ as a significant number of the groundwater samples fall along the SW-MWM while a few deviated. Three of the samples that plotted on the SW-MWM also have high conductivity, high $Cl^-/\sum$anions ratio, low $Na^+/(Na^+ + Cl^-)$ ratio and Cl^-/Br^- ratio close to 300 signifying seawater intrusion. Other samples plotting along this SW-MWM/Evaporative Water line show no other evidence of seawater intrusion. It is thus reasonable to assume that the observed deviation from the global meteoric water line is a result of evaporative enrichment of the stable isotope contents of the waters on the surface before groundwater recharge. Thus surface evaporation before recharge contributes significantly to groundwater salinisation in part of the Accra Plains. Carbon dating on the water samples were not carried out in the current study, however, previous tritium and carbon 14 dating of the Accra Plains indicates that groundwater gets older as one moves from the foothills of the Akwapim-Togoland Ranges toward the central part of the plains (Akiti 1986). This is consistent with the major ions chemistry whereby TDS increases from the foothills of the Akwapim-Togoland ranges toward the coast.

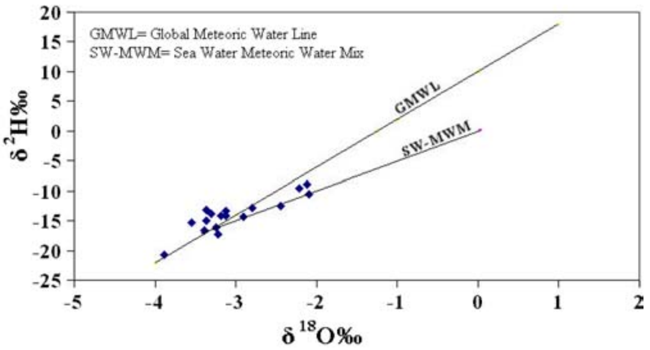


Fig. 11 Plot of δ^2 H versus δ^{18} O for groundwaters from the Accra Plains

Groundwater quality

The assessment of groundwater quality is based on the major ions, iron, pH and TDS. Groundwater along the foothills of the Akwapim-Togoland ranges is generally within the WHO (1993) guideline limits of the various major ions for drinking water quality. The pH of groundwater in this area is slightly acidic to neutral (5.8–7.0) but generally within the WHO (1993) guideline limits (6.5–8.5) for drinking water while total hardness is slightly to moderately high. For the aesthetic effect that it produces, World Health Organisation (WHO) decided to limit the concentration of iron in potable water to 0.3. However, an upper limit of 1.0 mg l^{-1} should suffice for most purposes (WHO 1993). The iron content in the groundwater in the Accra Plains is generally low with less than 3% of the wells having concentrations exceeding WHO upper limit. Thus groundwater along the foothills of the Akwapim-Togoland ranges is good for drinking. Elsewhere in the Accra Plains, TDS values outside the foothill of the Akwapim-Togoland ranges region are generally unsuitable for drinking purposes.

Conclusions

The chemical composition of groundwater in the Accra Plains is strongly influenced by halite dissolution from the soil zone; the processes that contribute to the concentration of major ions in the groundwater also depend on carbonate dissolution and precipitation, seawater intrusion, cation exchange, evaporative concentration of solutes and to minor extent aluminosilicates dissolution. Four main water types have been identified using the Expanded Durov Diagram. These are $Na\text{-}Mg\text{-}HCO_3$, Na-Cl, $Mg\text{-}Cl_2$ and/or $Ca\text{-}Cl_2$ and mixed water types. $Na\text{-}Mg\text{-}HCO_3$ water type occurs mainly close to the foothills of the Akwapim-Togoland Ranges to the north-northwest of the Accra Plains. This water type is mainly controlled by carbonate and aluminosilicates dissolution. Na-Cl water type occurs mainly in the centre of the plains and also along the coast. It is the

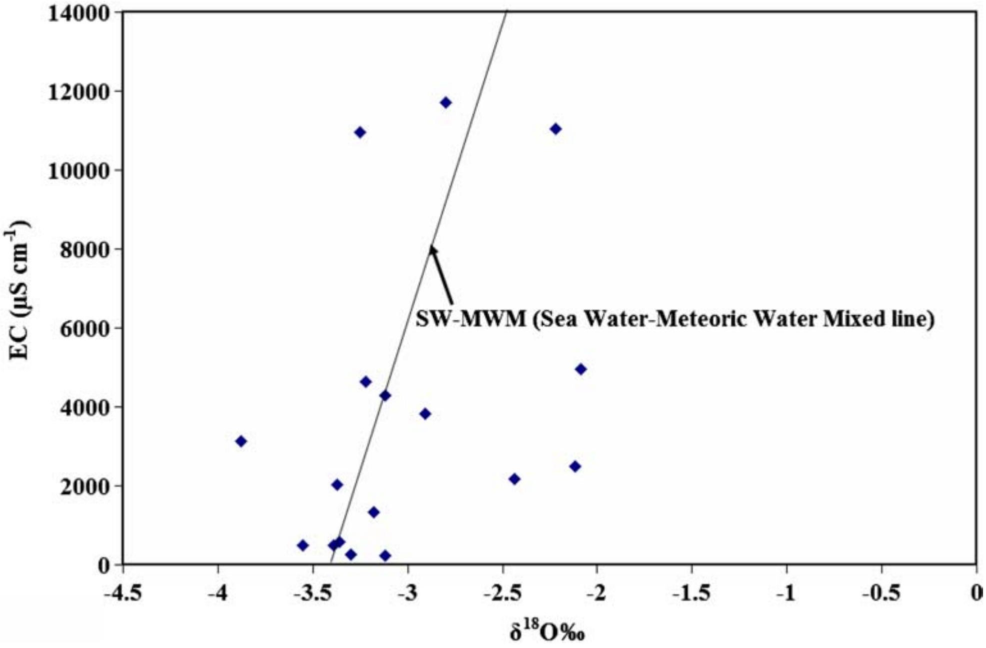


Fig. 12 Plot of EC versus δ^{18} O for the groundwater

dominant water type and is controlled mainly by halite dissolution and seawater intrusion. The existence of Ca-Cl_2 and Mg-Cl_2 water types close to the coast is confirmation of the occurrence of seawater intrusion and ion exchange.

Many of the groundwater samples plot along the meteoric water line suggesting direct integrative recharge. A few of the groundwater samples, however, plot along the meteoric water seawater mix line that is incidentally the evaporative line. Some of these samples have Cl^-/Br^- ratio close to 300 signifying seawater intrusion or having marine component. The rest of the samples that plot along the meteoric-sea water mix line have Cl^-/Br^- ratio significantly lower than 300 suggesting non-marine component and therefore must be due to evaporative concentration of solute.

Groundwater quality is generally good for drinking purposes along the foothills of the Akwapim-Togoland ranges. Elsewhere in the Accra Plains, groundwater quality is poor due to high TDS and individual solutes levels.

Acknowledgements I wish to thank Professor Niels O. Jorgensen for arranging for the isotope analysis at the Geological institute at the University of Copenhagen Denmark. This project was partly supported by the Water Research Institute (CSIR, Ghana).

References

Akiti TT (1980) Etude geochimique et isotopique de quelques aquifere du Ghana. Ph.D. thesis, Universite' de Paris-Sud

Akiti TT (1986) Environmental isotope study of groundwater in crystalline rocks of the Accra Plains. 4th Working Meeting Isotopes in Nature. Proceedings of an advisory group meeting. IAEA, Vienna, September 1986

Amuzu AT (1978) The quality of groundwater in the Accra Plains of Ghana. Unpublished Technical Report, Water Resources Research Institute (CSIR), Accra

Appelo CAJ, Postma D (1999) Chemical analysis of groundwater. geochemistry, groundwater and pollution. Balkema, Rotterdam

Barcelona M, Gibb JP, Helfrich JA, Garske EE (1985) Practical guide for groundwater sampling. Illinois State Water Survey ISWS Contract Report 374

Brady NC (1974) Th nature and properties of soils, 8th edn. Macmillan, New York

Brady PV, Walther JV (1989) Control of silica dissolution rates in neutral and basic solutions at 250C. Geochim Cosmochim Acta 53:2823–30

Brammer H (1967) Soils of the accra plains, Soil Research Institute. CSIR Memoir No. 3. Ghana

Claasen HC (1982) Guidelines and techniques for obtaining water samples that accurately represent the water quality for an aquifer. US geological survey open file report 82–1024 pp 49

Craig H (1961) Isotopic variations in meteoric water. Science 133:1702–1703

Davis SN, DeWiest RJM (1966) Hydrogeology. Wiley, New York, 463 pp

Dickson KB, Benneh G (1980) A new geography of Ghana. Longman, London

Durov SA (1948) Natural waters and graphic representation of their compositions. Dokl Akad Nauk SSSR 59:87–90

Freeze AR, Cherry JAQ (1979) Groundwater. Prentice-Hall, Englewood Ciffs, New Jersey 07632

Hounslow AW (1995) Water Quality Data Analysis and interpretation, Lewis, Boca Raton

Jankowski J, Acworth RI, Shekarforoush S (1998) Reverse ion exchange in a deeply weathered porphyritic dacite fractured aquifer system, Yass, New South Wales, Australia. In: Arehart GB, Hulston JR (eds) Proceedings of the 9th International Symposium. Water-rock interaction, Taupo, New Zealand, 30 March-3, Balkema, Rotterdam, April 1998:243–246

Junner NR, Bates DA (1945) Reports on the geology and hydrology of the coastal areas east of the Akwapim ranges. Ghana Geological Survey Memoir No. 7

Kess GO (1985) The mineral and rock resources of Ghana. Balkema, Rottendam

Kortatsi BK, Jørgensen NO (2001) The origin of high salinity waters in the Accra plains groundwater. In: First international conference on saltwater intrusion and coastal aquifers. Monitoring, modeling, and management. Essaouira, Morocco, April 23–25

Langmuir D (1971c) The geochemistry of some carbonate groundwaters in central Pennsylvania. Geochim Cosmochim Acta 35:1023–45

Langmuir D (1997) Aqueous Environmental Geochemistry. Prentice-Hall, New Jersey

Lloyd JW (1965) The hydrochemistry of the aquifers of north-eastern Jordan. J Hydrol 3:319–330

Lloyd JW, Heathcote JA (1985) Natural inorganic hydrochemistry in relation to groundwater. An introduction. Clarendon, Oxford

Mazor E (1976) Interpretation of environmental isotope and hydrochemical data in groundwater hydrology. Proceedings of an advisory group meeting, Vienna 27–31 January 1975. International Atomic Energy Agency, Vienna, 1976

Nii Consult (1998) Information building block. Ghana water management study. Unpublished Consultancy Report for the Ministry of Works and Housing, Ghana, DANIDA, World Bank

Nilsen R, Grammeltvedt G (1993) Chemical weathering of ore and host rock in six Norwegian sulphide mines. Norges geologiske undersokelse report 93.037, Ngu, Trondheim, Norway

Parkhurst DL, Appelo CAJ (1999) Phreeqc for windows version 1.4.07. A hydrogeochemical transport model. US Geological Survey Software

Quist LG (1976) A preliminary report on the groundwater assessment of the Accra Plains. Unpublished Technical Report, Water Resources Research Institute. CSIR, Accra

Sen Z, Al-Dakheel A (1986) Hydrochemical facies evaluation in Umm Er Radhuma limestone, Eastern Saudi Arabia. Groundwater 21:626–636

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

World Health Organisation (WHO) (1993) Guidelines for drinking water quality. Revision of the 1984 guidelines. Final task group meeting. Geneva 21–25 September 1992

WRRI (1996) Groundwater assessment report on the Accra Plains. Unpublished Technical Report, Water Resources Research Institute (CSIR) Accra