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Research Article

Hydrogeochemical Processes Influencing Groundwater Quality in the Black Volta Basin of Ghana

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Abstract: Hydrogeochemical processes influencing groundwater quality in the Black Volta Basin of Ghana have been studied. Groundwater samples were collected from 93 water points for physico-chemical analysis using standard methods. Major cation concentration was, generally, in the order of Ca^{2+}> Na^{+}>Mg^{2+}>K^{+} while major anion concentration followed the order HCO_3^->Cl^- >SO_4^{2-}. Mineral weathering (rock dissolution) and ion exchange were the controlling factors of groundwater composition. Stability diagrams show groundwater to be largely in equilibrium with Montmorillonite and Kaolinite and are quite reminiscent of climatic conditions pertaining to the geographical region of the basin. Ca-Mg-HCO_3 is the main groundwater type in the basin. Minor water types are Na-HCO_3 and Ca-Mg-SO_4. Principal Component Analysis (PCA), indicates that, HCO_3^- Ca^{2+}, Mg^{2+}, Na^+ and F^- contribute mainly to TDS and originate from the same-rock weathering.

Keywords: Anion, cation, chemical parameters, concentration, groundwater type, physical parameters

INTRODUCTION

Groundwater continues to be the major source of potable water supply especially in rural Ghana. Over long period, communities in the Black Volta Basin depend largely on the Black Volta and its perennial tributaries as well as dug wells for domestic and agricultural use. The combined effect of changing land use patterns and climatic change cause most of the perennial streams to become ephemeral. Dug wells also dry out in long spells of adverse or extreme dry weather. These results in water scarcity and its accompanying waterborne diseases particularly dracunculiasis or guinea worm (now eradicated), typhoid and schistomiasis (bilharzia). In order to control the incidence of waterborne diseases, the government of Ghana, with support from donor agencies particularly Canadian International Development Agency (CIDA) and non-governmental organizations, have put a number of groundwater development projects in place (Banoeng-Yakubo, 2000). However, some boreholes exhibit extremely low yield, deteriorating quality and a few even dry out within a few months after commissioning. Thus to manage the groundwater development in a sustainable manner, there is the need for the assessment.

The quality of this resource is influenced by many factors, including chemistry of the recharging water, the underlying geology, the vegetation and anthropogenic agents. Some minerals like carbonates dissolve quickly and change the composition of water faster, than other minerals like silicates which dissolve more slowly and have less conspicuous effects on the composition of water. Previous studies (Frape *et al*., 1984; Garrels and MacKenzie, 1967; Hem, 1985) have revealed that the chemistry of groundwater can often be traced to its reaction with the rock formation through which it flows.

A similar comprehensive study to understand the geochemistry of groundwater was undertaken in the Kulpawn sub-basin of the White Volta basin (Kortatsi *et al*., 2008). In spite of the importance of groundwater in the Black Volta basin, little is known about the natural processes and anthropogenic factors, which control the groundwater chemistry and affect the groundwater quality. The main objective of the paper, therefore, is the study of the hydrogeochemical processes influencing groundwater quality in the Black Volta Basin of Ghana.

STUDY AREA

The Black Volta has a total catchment area of 142,056 km^2, including areas outside Ghana - only

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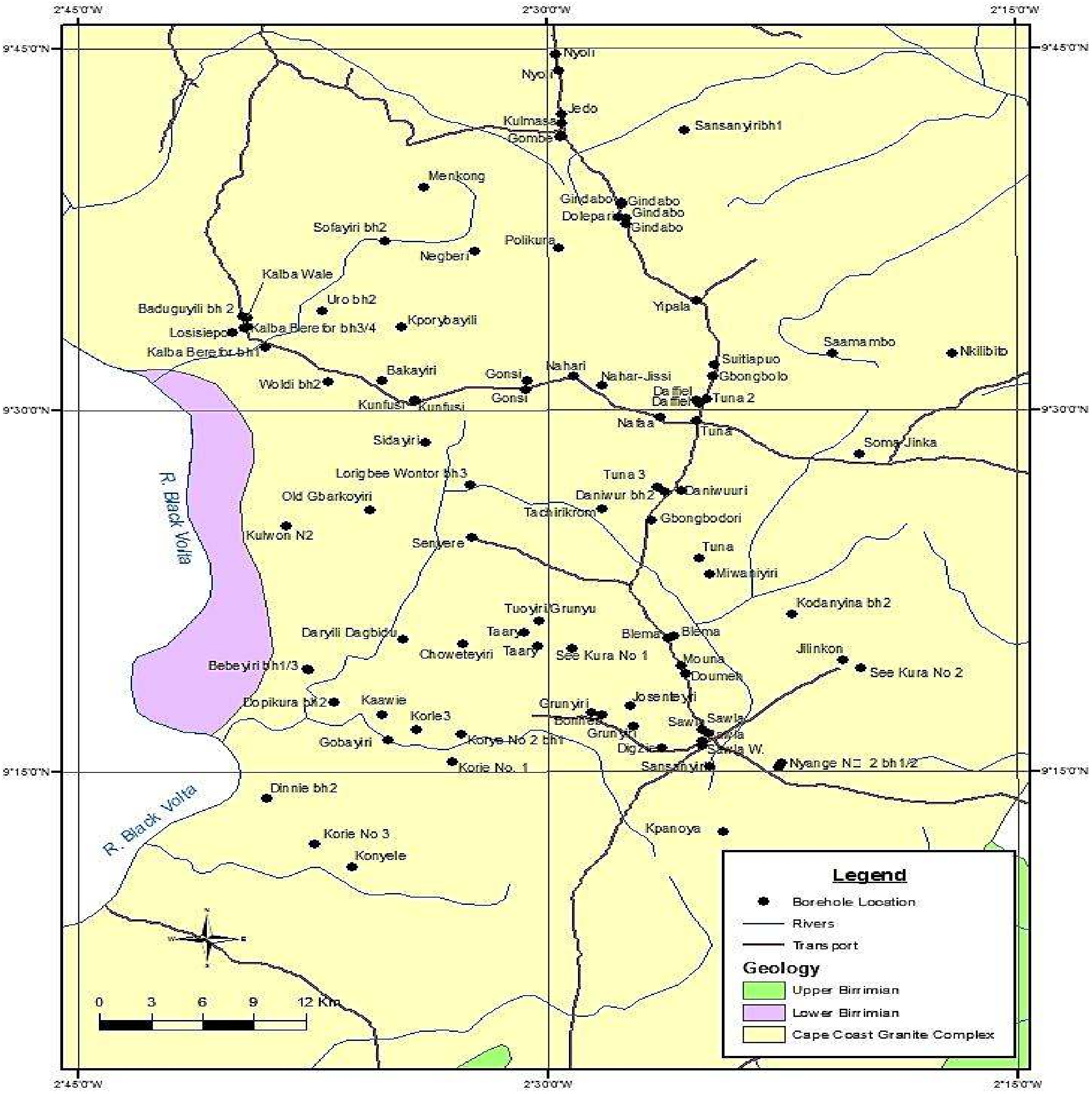


Fig. 1: Map of sampling area

33,302 km^2 (23.5%) of the catchment area is located in Ghana. The Black Volta basin is primarily located in north-western Ghana and includes portions of the Upper, Northern and Brong-Ahafo Regions of Ghana. Annual rainfall in the basin varies between about 1150 mm in the North and 1380 mm in the south. The major land use in the area is agriculture with food crop cultivation under extensive bush fallow. The main food crops include yam, cassava, maize, sorghum, millet, groundnuts and beans. Animal grazing on the free range is a significant activity (Barry *et al*., 2005).

The geology of the area consists predominantly of granitoids comprising of the Cape Coast and Dixcove granites, the Birimian and Voltaian systems and to a minor extent the Tarkwaian system (Kesse, 1985).

MATERIALS AND METHODOLOGY

Groundwater samples were collected from 93 sampling points (boreholes). The sampling points are indicated in Fig. 1. Sampling protocols by Wood (1981), Claasen (1982) and Barcelona *et al*. (1985) were followed. Groundwater samples were collected after pumping the well for approximately 7 min in order to purge the borehole of stagnant water (i.e., after temperature, pH and conductivity readings had stabilized). Samples for metals were filtered through 0.45 µm filters and preserved with 5 mL 6N (N is normality) HNO_3 in laboratory cleaned 100 mL high density linear polyethylene bottles. Samples for anion analyses were without preservation. Electrical conductivity and temperature were measured

Table 1: Statistical summary of physical and chemical parameters (mg/L except turbidity/NTU; conductivity/µs/cm; pH/pH unit; colour/TCU)

Parameter	Minimum	Maximum	Mean	Median	S.D.	WHO (2004)
Colour	2.50	150.00	5.65	2.50	17.02	
Turbidity	0.10	56.00	2.75	1.00	8.27	
Conductivity	84.80	1486.00	452.52	442.00	255.85	1500
Total Hardness	54.00	642.00	178.71	172.00	88.34	
pH	6.09	9.81	7.23	7.10	0.69	6.5-9.2
Total Alkalinity	50.00	422.00	196.58	202.00	76.79	
Ca^{2+}	8.00	131.00	34.66	32.10	21.03	200
Mg^{2+}	3.40	94.20	22.37	20.60	13.57	150
Na^{+}	6.30	93.10	30.07	27.90	18.35	200
K^{+}	0.40	12.40	4.48	4.45	2.29	200
HCO_3^{-}	61.00	515.00	239.94	249.00	93.14	240
SO_4^{2-}	1.60	246.00	14.64	6.05	27.97	250
Cl^{-}	3.00	131.00	18.16	9.90	21.16	250
NO_3^{-}	0.01	7.01	1.17	0.40	1.67	
PO_4^{3-}	0.001	0.914	0.108	0.075	0.125	
F^{-}	0.10	2.90	0.75	0.60	0.46	
SiO_2	4.60	215.20	62.23	61.90	20.49	

Min.: Minimum; Max.: Maximum; S.D.: Standard deviation

Table 2: Pearson correlation of major ions, TDS and conductivity

	TH	pH	TA	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SO_4^{2-}	Cl^{-}	SiO_2	HCO_3^{-}	NO_3^{-}	PO_4^{3-}	F^{-}
TH	1													
p H	0.102	1												
TA	0.730	0.418	1											
Ca^{2+}	0.787	0.060	0.569	1										
Mg^{2+}	0.808	0.109	0.625	0.310	1									
Na^{+}	0.214	0.446	0.596	0.256	0.095	1								
K^{+}	0.156	0.204	0.182	0.320	-0.045	0.229	1							
SO_4^{2-}	0.346	0.076	0.066	0.474	0.104	0.297	0.341	1						
Cl-	0.649	-0.006	0.304	0.624	0.443	0.264	0.257	0.376	1					
SiO_2	-0.134	-0.441	-0.405	-0.184	-0.087	-0.497	-0.119	-0.094	-0.147	1				
HCO_3^{-}	0.738	0.405	0.997	0.582	0.626	0.651	0.188	0.133	0.346	-0.404	1			
NO_3^{-}	0.090	-0.142	-0.050	0.115	0.039	-0.050	0.114	0.048	0.252	0.015	-0.058	1		
PO_4^{3-}	-0.034	-0.188	-0.166	-0.056	0.015	-0.166	-0.201	0.018	0.157	0.162	-0.162	0.017	1	
F^{-}	0.266	0.446	0.445	0.301	0.138	0.709	0.428	0.537	0.264	-0.326	0.506	-0.121	-0.133	1

TH = Total Hardness; TA = Total Alkalinity

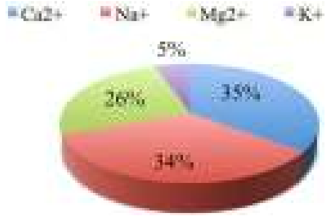


Fig. 2: Cation dominance pattern

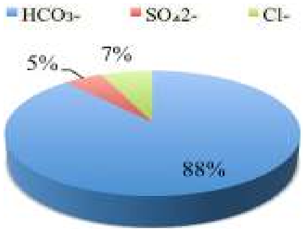


Fig. 3: Anion dominance pattern

simultaneously using the Universal Conductivity Meter MultiLine P4 set that had an in-built temperature compensation probe. The pH electrode was calibrated against pH 4, 7 and 10 buffers (Wood, 1981). Alkalinity was determined by titration in the field using Hach kit. Total hardness was determined by EDTA titration. All major ions Na^{+}, Ca^{2+}, Mg^{2+}, HCO_3^{-}, Cl^{-}, SO_4^{2-} as well as some minor elements K^{+}, NO_3^{-}, PO_4^{3-} and F^{-} were determined with Dionex DX-120 ion chromatograph at the Ecological Laboratory, University of Ghana. Silica was determined by colorimetric analysis with UV-visible spectrophotometer.

RESULTS AND DISCUSSION

The statistical summary of the results of physical and chemical parameters of tested samples of the study area are presented in Table 1.

Major ions dominance pattern: The concentrations of the major cations in the water samples were generally in the order $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and that for major anion concentrations followed the order $HCO_3^{-} > Cl^{-} > SO_4^{2-}$ as depicted by the Pie Charts in Fig. 2 and 3.

A plot of sodium against chloride gives a low correlation coefficient (Fig. 4), which is also confirmed by the Pearson correlation (Table 2). A 1:1 plot of Na^{+} versus Cl^{-} (Fig. 5) also shows a deviation where most points are plotted above the 1:1 line, indicating that

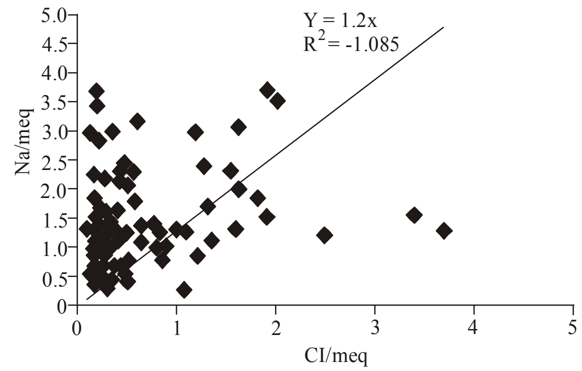


Fig. 4: Plot of Na against Cl

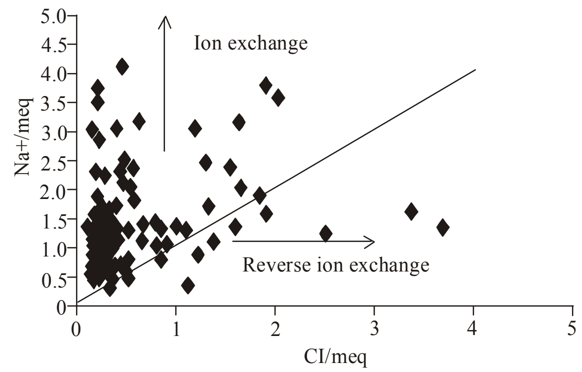


Fig. 5: A 1:1 plot of Na^+ against Cl

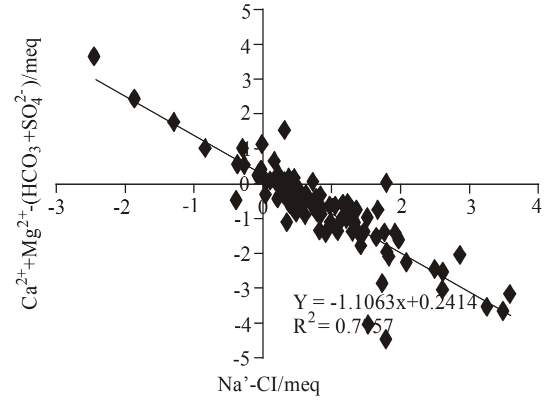
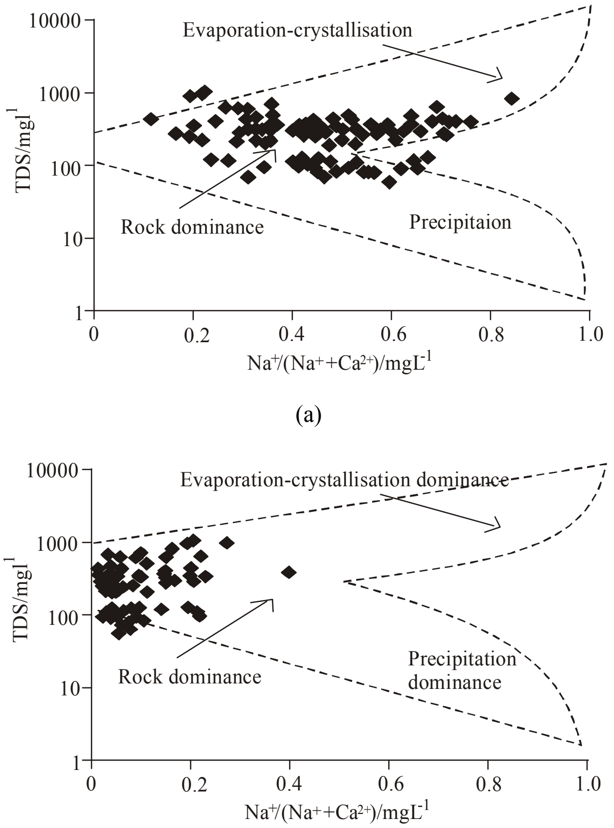


Fig. 6: Na-Cl against Ca+Mg-(HCO_3+SO_4)



(a)

(b)

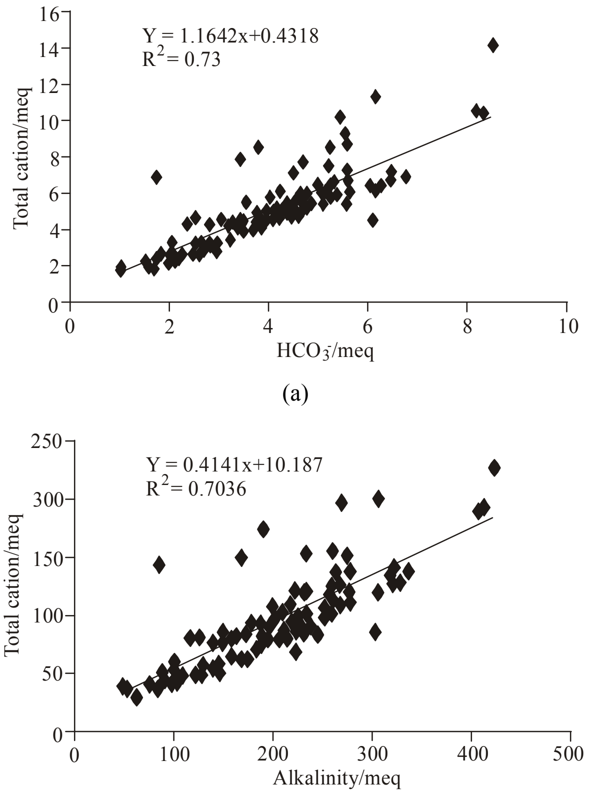
Fig. 7: (a): Gibbs plot of mechanism governing groundwater chemistry in the study area (Cation); (b): (Gibbs plot of mechanism governing groundwater chemistry in the study area (Anion)

most of the Na^+ is derived from other processes/sources than halite dissolution.

Cation exchange is also a regulatory factor of ionic concentrations in water. It plays an important role as a temporary buffer when ionic contents are variable, leading to non-steady-state conditions (Gimenez and Morell, 1997). The plot of Na^+ against Cl^- (Fig. 4) indicate an increase in sodium ions, without a corresponding increase in chloride concentration and this can be explained by ion exchange process where Ca^{2+} and Mg^{2+} are removed from solution and being replaced by Na^+ ions. Sodium concentration in groundwater in the Black Volta Basin may, therefore, be partly influenced by ion exchange processes. If ion exchange is the controlling factor of groundwater composition, a plot of Na-Cl against Ca+Mg-(HCO_3+SO_4) will have a negative slope of unity (Fisher and Mullican, 1997). Figure 6 shows plot of Na-Cl against Ca+Mg-(HCO_3+SO_4), with a slope of -1.1, which is a confirmation of the role of ion exchange in the Black Volta basin.

Gibbs plots (Gibbs, 1970) as in Fig. 7a and b showed that rock (silicate) weathering is the predominant hydro geochemical process controlling the groundwater in the study area.

Kim *et al*. (2004) suggested that a 1:1 ratio between total cation and alkalinity is an indication that mineral weathering is the major process affecting groundwater chemistry. Figure 8a and b show a plot of total cation against bicarbonate alkalinity and total alkalinity respectively, with strong positive correlations (r = 0.73; 0.70), indicating that mineral weathering might be the major process contributing to ionic concentrations of the groundwater in the Black Volta basin of Ghana. This confirms that silicate weathering is taking place alongside cation exchange.



(a)

(b)

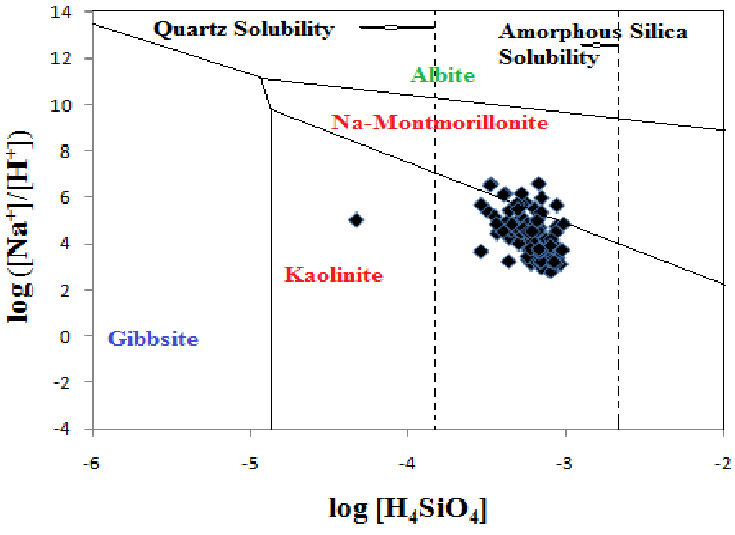
Fig. 8: (a): Gragh of total cation against HCO_3 alkalinity; (b): Total cation against total alkalinity

Potassium-bearing minerals such as microcline and illites-sericites are very resistant to solution and potassium is preferentially incorporated into clay minerals. Potassium concentration in groundwater is higher in agricultural areas. Livestock production constitutes an important component of the economy of the Black Volta basin, particularly in the savannah areas of Northern and Upper West regions. K^+ and NO_3^- concentration could be attributed to farming and livestock production. This is evident in the fairly positive loading for K^+ and NO_3^- in the component 3 of the Principle Component Analysis (Table 3). There is, however, low correlation between potassium and nitrate (Table 2). This raises issues about the sources of potassium. There is weak correlation between K^+ and other major cations (Table 2). These correlation coefficients suggest that the K^+ could be derived from K-feldspars ($KAlSi_3O_8$).

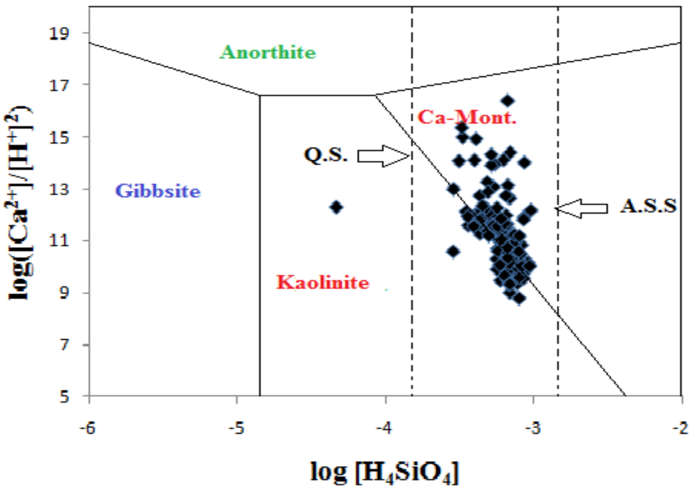
Plots of Na^+/H^+ and Ca^{2+}/H^+ stability diagram for the ground waters of the Black Volta Basin, show them to be largely in equilibrium with montmorillonite and Kaolinite (Fig. 9a and b).

Table 3: Principal components

	Component		
Variable	Component 1	Component 2	Component 3
Conductivity	0.944	0.214	0.111
TH	0.829	0.320	-0.330
pH	0.492	-0.582	0.129
TA	0.948	-0.193	-0.132
Ca^{2+}	0.662	0.535	0.083
Mg^{2+}	0.668	0.059	-0.546
Na^+	0.685	-0.352	0.328
K^+	0.404	-0.045	0.650
HCO_3^-	0.943	-0.164	-0.155
SO_4^{2-}	0.295	0.562	-0.043
Cl^-	0.240	0.736	0.266
NO_{3-}	-0.220	0.240	0.508
PO_4^{3-}	-0.188	0.277	-0.276
F-	0.746	-0.364	0.184
SiO2	-0.277	0.524	0.122
TDS	0.944	0.214	0.111
Eigen values	6.879	2.412	1.482
% Variance	42.995	15.077	9.265



(a)



(b)

Fig. 9: (a): Silicate stability diagram Na-Al-Silicate; (b): Silicate stability diagram Ca-Al-Silicate

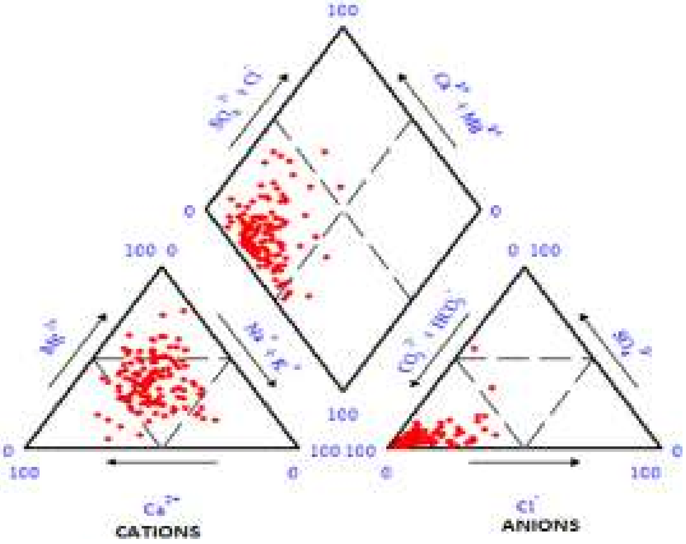


Fig. 10: Trilinear Piper diagram for groundwater in the Black Volta Basin

From the analysis of the chemical plot in the triangular field of the trilinear piper diagram (Fig. 10) and considering cation plot field (triangle on the left), approximately 69% of the groundwater samples plot mainly in the middle, which suggests mixed cations with no dominant cation type. Calcium and magnesium constitute 22% whereas Na/K contributes 5%. However, in the anion plot field (triangle on the right), almost all the samples (about 98%) plotted towards the HCO_3^- corner, which suggests HCO_3^- as the predominant anion and the groundwater having a short residence time. There is, therefore, one major water type in the Black Volta Basin which is Ca-Mg-HCO_3. Minor water types in the basin are Na-HCO_3 and Ca-Mg-SO_4. The groundwater samples plotting in the Ca-Mg-HCO_3 dominant of the diamond field suggest active recharge, short residence time and temporary hardness. This type of waters usually has chemical properties, which are dominated by alkaline earths and weak acids and apparently not associated with a particular geological formation.

PRINCIPAL COMPONENT ANALYSIS

Principal Component Analysis (PCA), as stated by Harman (1976) reduces a large data set to give a simple interpretation. In the hydrochemistry field, these techniques are widely used because they have several advantages over traditional graphical approaches (Dalton and Upchurch, 1978). The number of components to keep was based on the Kaiser criterion, for which only the components with eigenvalues greater than 1 are retained (StatSoft Inc., 2004).

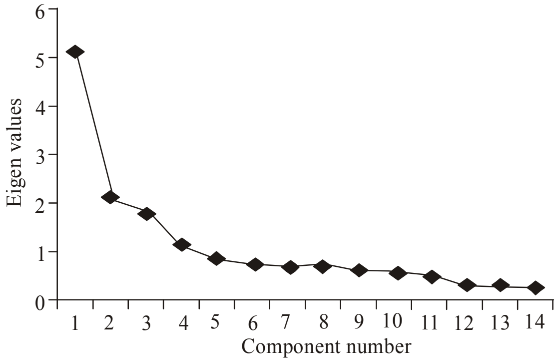


Fig. 11: Eigen values versus component number

Each of the three components has eigen value > (greater than) 1 (one) and they account for percentage variance of 67.34 whereas the other unextracted components have eigen values < 1 (i.e. less than one) and accounts for a percentage variance of 32.66.

The number of eigen values can be estimated from the screen plot (Fig. 11). In Fig. 11, the eigen values sharply decrease within the first three components and then slowly stabilizes for the remaining ones. TDS, EC, TA, TH, HCO_3^-, show high positive loading (0.829-0.948). This reveals the TDS as a function of EC. It also shows that HCO_3^- contributes high percentage of the total dissolved solids in the basin. The concentrations of Ca^{2+}, Mg^{2+}, Na^+ and F^- show moderate positive loading (0.662-0.746) in the first component (Table 3). Silicate weathering could be the factors influencing the high positive loading of Ca^{2+}, Mg^{2+} and Na^+. There is low correlation between Ca^{2+} and SO_4^{2-} (0.474) suggesting both ions may not have originated from the same source. The high loading of Cl and relatively moderate loading of SO_4 in the second component suggests impurities at source or an impure source. The moderate loading of Ca^{2+} and SiO_2 might be due to the dissolution of Ca-silicate minerals. The relatively higher correlation between Ca^{2+} and Cl^- (0.624) might be due to ion exchange processes. The third component is governed by K and NO_3- and is attributable to anthropogenic activities in the basin but the low correlation between K and NO_3- suggest different sources.

CONCLUSION

The concentrations of the major cations in the water samples were generally in the order of Ca^{2+}> Na^+>Mg^{2+}>K^+. The major anion concentrations followed the order HCO_3^->Cl^- >SO_4^{2-}. Increase in sodium ions, without a corresponding increase in chloride concentration can be explained by ion exchange process where Ca^{2+} and Mg^{2+} are removed from solution and being replaced by Na^+ ions. The concentration of cations in the Black Volta Basin is, therefore, partly influenced by ion exchange processes. A strong positive correlation (r = 0.73) for total cation against bicarbonate alkalinity and against total alkalinity also indicate mineral weathering as a possible major process contributing to ionic concentrations of the groundwater in the Black Volta basin of Ghana. Plots of Na^+/H^+ and Ca^{2+}/H^+ stability diagram for the groundwaters of the Black Volta Basin show them to be largely in equilibrium with montmorillonite and Kaolinite. Potassium (K^+) and NO_3^- concentration could be attributed to farming and livestock production. This is evident in a high loading for K^+ and NO_3^- in the component 3 of the Principle Component Analysis table. There is a weak correlation between K^+ and other major cations (Table 3). These correlation coefficients suggest that the K^+ could also be derived from K-feldspars ($KAlSi_3O_8$).

From the analysis of the chemical plot in the triangular field of the trilinear piper diagram, there is one major water type in the Basin-Ca-Mg-HCO_3. Minor water types are Na-HCO_3 and Ca-Mg-SO_4.

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