Hydrochemistry and evaluation of groundwater suitability for irrigation and drinking purposes in the southeastern Volta river basin: manya krobo area, Ghana

E. A. Kaka[1,2], T.T. Akiti[2]. V.K. Nartey[2,3], E.K.P. Bam[1,2] and D. Adomako[1]

[1]National Nuclear Research Institute, Ghana Atomic Energy Commission, P.O. Box LG 80, Legon-Accra, Ghana

[2]Graduate School of Nuclear and Allied Sciences, University of Ghana, P. O. Box AE 1, Legon-Accra, Ghana

[3]Department of Chemistry, University of Ghana, P. O. Box LG 58, Legon-Accra, Ghana.

ARTICLE INFO

ABSTRACT

The Manya Krobo area is bounded in the east by Lake Volta which resulted after the construction of the Akosombo dam since 1965. The groundwater quality of 25 samples in the study area was evaluated for its suitability for drinking and irrigation purposes by estimating pH, EC, TDS, hardness and alkalinity besides major ions, isotopes, SAR, % Na, RSC, RSBC, chlorinity index, SSP, non-carbonate hardness, Potential Salinity, Permeability Index, Magnesium hazard and Index of Base Exchange. The percentage sodium, sodium absorption (SAR), and residual sodium carbonate (RSC) indices show that the groundwaters are generally suitable for irrigation purposes. Negative Index of Base Exchange indicates the chloro-alkaline disequilibrium in the study area and all the water samples fall in the rock dominance field based on Gibbs' ratio. Based on total hardness, the groundwater in the area is soft. Na-K-HCO$_3$-Cl (48%), Na-HCO$_3$ (40%), and Na-Cl (12%) water types were delineated from the area. Stable isotope analysis of water samples indicates meteoric origin of recharge.

Introduction

Groundwater is almost globally important for human consumption as well as for the support of habitat and for maintaining the quality of base flow to rivers. Being naturally filtered in their passage through the ground, they are usually clear, colorless, and have excellent quality, being free from microbial contamination and require minimal treatment (Babiker, et al., 2007). Unfortunately, it seems that we can no longer take high quality groundwater for granted, as a threat is now posed by an ever-increasing number of soluble chemicals from urban development, industrial activities and modern agricultural practices (Ravikumar and Somashekar, 2010). In Ghana, groundwater is increasingly gaining eminence as an alternative source of water in both rural and urban communities for various uses. A number of reasons account for this development. First, aquifers underlie almost all communities in Ghana and groundwater can be abstracted at relatively shallow depths. Second, groundwater is relatively cleaner and does not need extensive treatment before use. Third, most surface water bodies run out during long spell of dry season (Yidana, 2010). However, it is impossible to control the dissolution of undesirable constituents in the waters after they enter the ground (Johnson 1979; Sastri, 1994). Hence, the investigation/assessment of geochemical element distribution and the natural background of these resources are of paramount importance in reconciling the exploitation of surface water and groundwater with the protection of the environment, including the well being of both mankind and local fauna and flora (Darnley et al., 1995; Edmunds et al., 2002). A few studies on hydrochemical characterization and evaluation of groundwater have been carried out in the different parts of the Volta River basin in Ghana (Kortatsi et al. 2008; Yidana et al. 2008; Acheampong and Hess; 1998). Even though the study area is agrarian groundwater has not been studied in great detail for the various uses and hence the effort in the current paper to assess groundwater quality through hydrogeochemical analysis to determine suitability for domestic and irrigational purposes.

Study area

Location

The study area is largely located in Upper Manya Krobo District of the Eastern Region. The Upper Manya Krobo District is located at the North-Eastern corner of the Eastern Region of Ghana and lies between latitudes 6.2-6.50N and Longitudes 0.3 - 0.00 W of the Greenwich Meridian. The major towns in Upper Manya area are Asesewa, Sekesua, Akateng and Otrokper.

Land use in the study area is agriculture, mainly subsistence crop production and animal husbandry. Crops principally grown include maize, millet, cassava, yam, cocoyam, sweet potato, sugar cane, tomato, okra, bambara beans, plantain, banana, groundnut and cowpea.

Varieties of herbicides are also employed in preparing farmlands and weed controls. Inorganic fertilizer and other agrochemical are sparingly used in the area. Livestock and poultry farming is mainly semi intensive.

The undulating topography of the area ranges between 660 meters above sea level in the south-western part of Sekesua and about 50 meters above sea level at margins of the Volta Lake. Seasonal rivers such as the Ponpon, Krum, Dawado, Ayermesudo, Anyaboni, Fefedo, Pleyo, Dawdo and Aboasa exhibit trellised pattern of flow towards the Lake.

Tele:
E-mail addresses: e.longbridge@yahoo.com

The area experiences two major seasons, namely wet and dry seasons. The rainy season exhibits double maxima: the main rainy season occurs between April and July, whilst the minor one falls between September and October of every year. The dry and warm season are experienced from November to March.

Geology and hydrogeology

The area under study is underlain by rocks of the Voltaian Super-group and the Buem structural unit (Fig 1.) The Voltaian Super Group is made up of Neo-proterozoic to Early Cambrian, lithologically diverse platform sediments. There are few detailed geologic descriptions of sediments of the Voltaian Group sequences; subdivision of the group is difficult due to poor exposure and the lack of laterally persistent lithological marker beds or fossils (Anani, 1999). The group has generally been divided into three formations, each separated by an unconformity marked by a tillite (Fig. 2). The Lower Voltaian Formation consists of a massive tocross-bedded arkosic sequence. The Middle Voltaian Formation consists of a flyschoid sequence, and the Upper Voltaian Formation consists of a molasse sequence (Affaton et al., 1980). The Lower Voltaian Formation unconformably overlies the Birimian Supergroup.
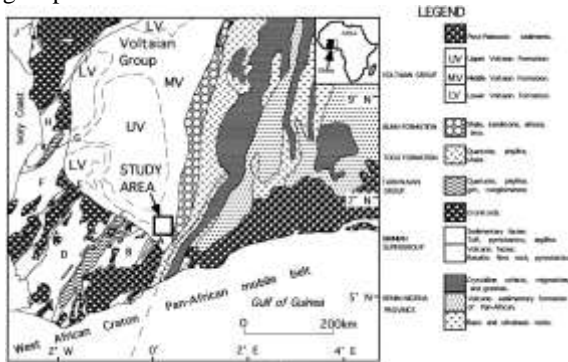

Figure 1 Generalized geological map of the West African Craton. Modified after Ako and Wellman (1985) Belts and basins in the Birimian are defined after Leube et al. (1990) as follows: *A* = Kibi–Winneba belt; *B* = Cape Coast Basin; *C* = Ashanti belt; *D* = Kumasi Basin; *E* = Sefwi belt; *F* = Sunyani basin; *G* = Bui belt; *H* = Maluwe Basin; *I* = Bole–Navrongo belt; *J* = Lawra belt.

The Middle Voltaian Formation overlies the Lower Voltaian Formation with a slight angular unconformity. Conglomeratic beds interpreted as tillites form the basal part of the Middle Voltaian Formation (Petters, 1991). Shales, siltston.es and sandstones, glauconitic in part, constitute the principal lithologies of the Middle Voltaian Formation. The Upper Voltaian Formation is divided into a lower and an upper unit. The lower unit consists mostly of dirty-yellow, fine-grained, thinly bedded, micaceous, feldspathic quartz sandstones with subordinate argillite intercalations. The upper unit consists of white to whitish-yellow, massive, fine- to medium-grained, cross-bedded arkosic and quartzose sandstones. The Upper Voltaian Formation occurs as scattered outcrops in the central part of the Voltaian Basin, with an average thickness of about 400m.

Hydrostratigraphic units of the Voltaian group are identified as Anyaboni and Kwahu sandstone Members (Saunders, 1970 and Anani, 1999) (Fig. 2). Borehole success rate in the area is about 56% and well depth ranges between 222.0 and 55.0 metres. Mean static water level in the area is 6.6m. The average borehole yield is 8.5m^3/h (Dapaah-Siakwan and Gyau-Boakye, 2000). Aquifer transmissivity values in the area fall within the

range of 0.18–197.7 m^2/day with a mean of 21 m^2/day (Yidana et al., 2008).

A few localities in the study area are situated in the lower part of the Middle Buem Member of the Buem Formation. The Buem formation consists of a thick sequence of shale, sandstone, and volcanic rocks with subordinate limestone, tillite, grit and conglomerate. The sandstones overlie the basal beds of shale and the conglomerate and tillite overlie the sandstone. (Dapaah-Siakwan and Gyau-Boakye, 2000).
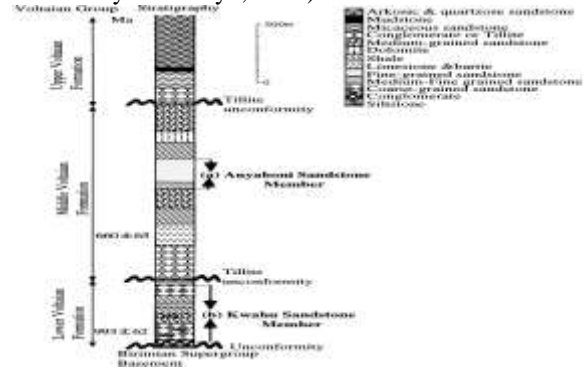
Figure 2 Sequence of the Voltaian Group indicating horizons of both the Kwahu Sandstone Member and the Anyaboni Sandstone Member (redrawn after Cahen et al., 1984 and Petters, 1991)

Rocks of the Buem formation are largely inherently impervious, but fracturing and weathering create secondary permeability in them at some locations to form high yielding aquifers.

The success rate for obtaining water from boreholes in the Buem structural unit is about 88%. Boreholes are drilled to an average depth of 65 m in sandstone. The average yield from these boreholes is about 9.2 m^3/h; ranging from 0.72–24.3 m^3/h. The higher-yielding boreholes in this area probably tap large fracture systems or fault zones (Dapaah-Siakwan and Gyau-Boakye, 2000).

Methodology

A total of 33 water samples (25 groundwater, 3 streams and 5 locations along the Volta Lake) were collected across the catchment during the periods of September, 2009. The geographical location of all sampling sites was recorded using a hand-held global positioning system (GPS) (Figure 3).

Field investigations

Alkalinity and physical parameters such as electrical conductivity (EC), total dissolved solids (TDS), temperature and pH of the samples were measured in the field using Hatch field titration kit and portable EC and pH meters. For groundwater samples, boreholes were purged until stable readings for the physical parameters were obtained.

Samples were subsequently filtered through 0.45 micron membranes and collected in acid-washed, well-rinsed polyethylene bottles. Filtered and acidified (1% v/v HNO$_3$) samples were used for major cations, while filtered unacidified samples were used for anion analysis. Unfiltered water samples (surface water and groundwater) were collected in 30-ml glass bottles and tightly sealed for stable isotopes analysis.

Laboratory analyses

Chemical and isotopic analysis of the water samples was performed at the National Nuclear Research Institute, Ghana Atomic Energy Commission. Calcium and magnesium ions were analyzed using Varian AA240 Fast Sequential Atomic Absorption Spectrometer. Sodium and potassium ions were also measured using flame emission photometer (Sherwood model

420). The sulphate and nitrate ions were analyzed using a UV-Visible spectrophotometer (Shimadzu). The chloride ion concentrations in the water samples were determined by titration. Stable isotopes of oxygen and hydrogen were determined using isotope mass spectrometry.

An off-axis integrated cavity output spectroscopy (OA-ICOS) Los Gatos Research DT-100 Liquid-Water Isotope Analyser (Model 908-008-2000) was used to measure δ^2H and $\delta^{18}O$ of the water samples (IAEA-TCS-35, 2009). The analytical reproducibility was $\pm 0.2\%$ and $\pm 1.0\%$ for the oxygen and deuterium, respectively.
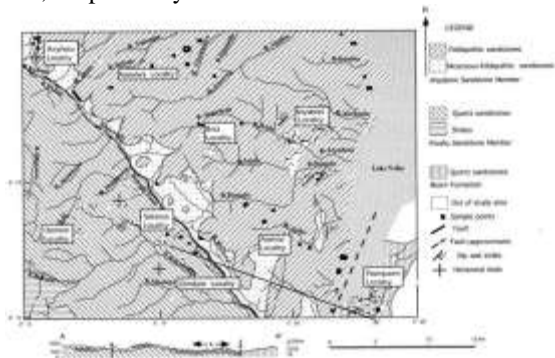
Figure 3 Sampling localities with the Geological map of the Voltaian Group and the Buem Formation in the southeastern part of the Voltaian Basin See insert map in Fig. 1 for location

Result and discussion
General parameters

The results of non-ionic parameters (temperature, Eh, pH, EC, TDS, and salinity) and concentrations of major ions (Ca^{2+}, Mg^{2+}, Na^+ and K^+, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-) measured in the 25 groundwater samples are presented in Tables 1 and 2 respectively.

The pH of the groundwater in the study area varies from 5.20 to 6.92. These could be described as moderately acidic waters. However, all the samples fall within the natural water pH range of 4.5–7.0 (Langmuir, 1997).

Groundwater samples at Oterkpolou, Bormase-Tenya-1 and Bormase- Tenya-2 all in the Abetifi formation, and also at Seseaman-Kperti, Seseaman Sisi, Brepaw Kperti all in Anyaboni formation had pH below 6.5. However, the WHO (1996) recommended pH range for water portability is 6.5-8.5. The slightly lower pH values of these water samples could be due to geology of the area. Decay of vegetation or hydrolysis of iron or aluminium could also contribute to acidic waters.

Oxidation potential (Eh) of the groundwater samples have ranges between -33.5 and 70.8mV. The sign of the potential is positive if the reaction is oxidizing and negative if it is reducing. About 84% of the samples have negative Eh potentials.

Eh correlates linearly (but negatively) with pH strongly ($r^2 = 0.99$) and varied narrowly suggesting interdependence of Eh and pH in the area. A plot of Eh vrs pH for all the water samples shows values concentrating near the lower limit of the diagram. This indicates reducing environment in the subsurface of the groundwaters.

The conductivity of water within a temperature range 25.3 – 29.4^0C had a range of 125.3 to 2970 $\mu S\ cm^{-1}$ with mean and median values of 614.96 and 286.00 $\mu S\ cm^{-1}$ respectively.

Six boreholes had conductivity values above 1000 $\mu S/cm$. All these boreholes are located in either in Buem or Afram formations that contain limestone suggesting lithology is contributing factor for quality of water in the area. Moderately low conductivities occur in the Anyaboni formation of the Voltaian terrain and may be attributed to short residence time of the groundwater hence little dissolution of aquifer materials.

The total dissolved solids (TDS) in the groundwater vary from 53.7 to 1274.0 mg/L. The mean TDS is 261.7 mg/L. The lowest TDS occurs in borehole at Sekeswa, which has the highest altitude of 342m in the study area. The highest value of 1274mg/L occurs in borehole at Oborpa West in the extreme southern section. Areas of low TDS are said to be the recharge areas and normally referred to as young waters, whereas areas of high TDS are described as discharge areas and referred to as old waters.
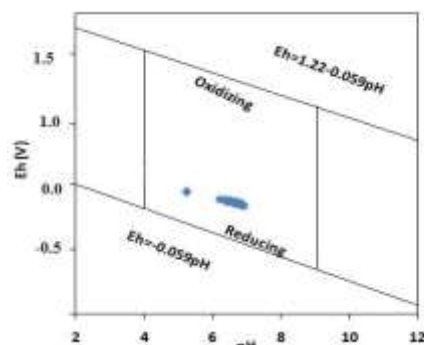
Figure 4: The Eh-pH relationship of water samples collected at study area

A plot of well elevation versus conductivity (Figure 5) shows that low conductivities are found at higher elevations and higher conductivities found at lower elevations near the bank of the lake. The low conductivities can be due to short residence time at high altitude. High conductivity also means long residence time. This may also indicate that groundwater is recharged at higher altitude and flows towards the lake hence more ions get dissolved at discharge area.
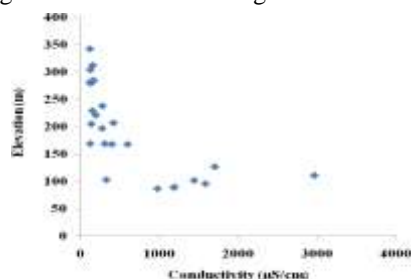
Figure 5 Plot of well elevation versus conductivity

Major ion chemistry

Concentration of major ions (Ca^{2+}, Mg^{2+}, Na^+ and K^+, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-) are also generally low (Table 2).

To verify the analytical error of analyzed ion concentration, electroneutrality (ionic balance) was computed by following equation:

$$E = \frac{\Sigma cation - \Sigma anion}{\Sigma cation + \Sigma anion} \times 100 \qquad (1)$$

where the sum of major cations and anions are expressed in meq/L and E is the error percent/reaction error/ cationic and anionic balance. The ionic balances for the analyses varied from -5.9 to 7.9%. The reaction error of all groundwater samples was less than the accepted limit of $\pm 10\%$ (Hem, 1975) and an added proof of the precision of the data.

Na^+ is relatively the dominant cation with range between 21.3 mg/L at Sekeswa to 733.0mg/L at Oborpa West. The mean and median concentrations are 143.5 and 54.6 mg/L

respectively. Weathering of plagioclase feldspars (albite) could be a possible source of sodium in the groundwater in the area following the reaction equation:
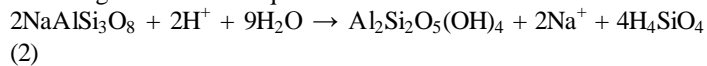
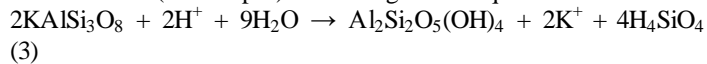$$2NaAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4 \quad (2)$$
(albite)

K^+ concentrations in the groundwater samples were also found to be relatively high ranging from 7.8-78.0mg/L with mean and median levels of 32 and 24.3mg/L respectively. K^+ in the groundwater samples might also be as a result of weathering of orthoclase (K-feldspar) according to the equation:

$$2KAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 4H_4SiO_4 \quad (3)$$
(K-feldspar)

However, it is worthy to note the excess of Na^+ over K^+ perhaps because K-feldspar in the area is more resistant to weathering than albite.

Mg^{2+} concentration in the groundwater also ranges from 0.96-18.04mg/L with mean and median values of 5.46 and 4.22mg/L respectively. Dolomite in the sedimentary rocks of the area might be the source of the Mg^{2+} in the groundwater samples.

Ca^{2+} is the least prevalent cation whose concentration ranges between 5.1 and 12.8mg/L with mean value of 7.7mg/L.

Ca^{2+} might be released into groundwater when calcium rich minerals such as calcite and anorthite undergo weathering. The release of Ca^{2+} into groundwater during anorthite weathering may be represented by the equation:
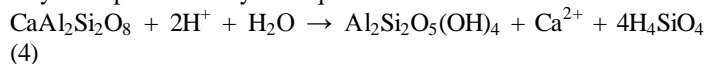
$$CaAl_2Si_2O_8 + 2H^+ + H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 4H_4SiO_4 \quad (4)$$
(Anorthite)

The low concentrations of Ca^{2+} and Mg^{2+} might be due to natural softening by cation exchange, mostly by Na^+ rich clays displacing Ca^{2+} and Mg^{2+} in solution as illustrated by the equation below:

$$CaCO_3 + H_2CO_3 + 2Na_{ex} \rightarrow Ca_{ex} + 2Na^{2+} + 2HCO_3^- \quad (5)$$

HCO_3^- is the dominant anion in the groundwater samples from the area with concentration ranging between 72 and 712mg/L and median value of 193.8mg/L. The anion forms approximately 57% of anion content of the samples. Natural sources such as reaction of carbonate minerals with carbon dioxide gas (CO_2) and the dissolution of CO_2 from the possible mechanisms may supply bicarbonate into groundwater according to the equations:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \quad (6)$$
$$CO_2 + H_2O \rightarrow H^+ + HCO_3^- \quad (7)$$
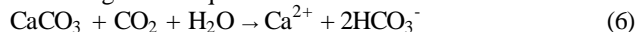
The higher HCO_3^- concentrations (380-712mg/L) in the area are found in the Buem and the part of Anyaboni hydrostratigraphic formations of plain land near the Volta Lake which contain limestone as earlier stated under the geology of the area, suggesting carbonate mineral dissolution as the major source of HCO_3^- in the groundwater samples.

Cl^- concentration in groundwater ranges between 4.0 and 699.8mg/L with mean and median values of 121mg/L and 38mg/L respectively. The ion forms approximately 42% of the anion contents. A good correlation between HCO_3^- and Cl^- ($r^2 = 0.8$) is an indication of similar processes responsible for the presence of the two ions in groundwater in the area. Besides, sea aerosol sprays and precipitation are possible sources of Cl^- in the groundwater especially in the southern portions of the study area.

NO_3^- has low concentrations in the groundwater samples ranging from 0.0 to 4.39mg/L with mean and median values of 0.9 and 0.5mg/L respectively. The low NO_3^- in groundwater could mean that there is little or no pollution of the resource or the geology of the area does not contain the anion. Fertilizer and sewage is possible sources nitrate in groundwater. However, application of fertilizer was not seen as the farmers in the area remarked the land is fertile and no need for the practice. The area is also rural so sewage was not conspicuous.

The SO_4^{2-} concentration in the groundwater samples is also low. It ranges from 0.077 to 6.64mg/L. The mean concentration is 1.17mg/L while the median concentration is 0.51mg/L. The low levels of SO_4^{2-} in the groundwater in the catchment might be a pointer to the fact that of sulphate minerals are absent in the aquifer materials.

The order of magnitude of cations in the samples is $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$ and that of anions is $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$.

Based on Cl, SO_4, HCO_3 concentrations, the groundwater sources can be categorized as normal chloride (<15meq/L), normal sulfate (<6 meq/L) and normal bicarbonate (2–7 meq/L) water types (Soltan, 1998). Among the 25 groundwater samples, about 92% and 100% samples respectively were categorized as normal chloride and normal sulfate, while only 56% of samples were of normal bicarbonate type.

Hydrochemical facies

To know the hydro-geochemical regime of the study area, the analytical values obtained from the groundwater samples are plotted on Piper (1994) tri-linear diagram. These plots include two triangles, one for plotting cations and the other for plotting anions. The cation and anion fields are combined to show a single point in a diamond-shaped field, from which inference is drawn on the basis of hydro-geochemical facies concept. These tri-linear diagrams are useful for bringing out chemical relationships among groundwater samples in more definite terms rather than with other possible plotting methods. Facies are recognizable parts of different characters, belonging to any genetically related system. Hydrochemical facies are distinct zones that possess cation and anion concentration categories and this concept helps to understand and identify the water composition in different classes. To define composition class, Back and Hanshaw (1965) suggested subdivisions of the tri-linear diagram (Figure 5) to define composition class, based on which the interpretation of distinct facies from the 0 to 10% and 90% to 100% domains on the diamond-shaped cation to anion graph is more helpful than using equal 25% increments.

The Piper tri-linear graphical representation of chemical data of representative samples from the study area reveal the analogies, dissimilarities and different types of waters in the study area, which are identified and listed in Table 3. This clearly explains the variations or domination of cation and anion concentrations during the season.

The Na-K type of water predominated during post monsoon of September, 2009 accounting for 100% of the samples. Similarly, for anion concentrations, the HCO_3-type of water predominated in 88% samples.

Variations in hydrochemical facies in the samples collected from the Manya Krobo area are given in Table 4. Three principal hydrochemical water types have been delineated. These are mixed $Na–K-HCO_3-Cl$ water types. In this water type, no particular anion predominates while Na^+ is the main cation. The principal water type depicts rock–water interaction

involving the dissolution of carbonates and feldspars by the recharging groundwater within the relatively permeable weathered zone above the underlying rocks.

Na-HCO$_3$ is the second water type (III section of the diamond shape) which suggests there is base-exchanged aggressive recharging alkali carbonates water. Chemical evolution of Na-HCO$_3$ water type in the Manya Krobo area along the Volta Lake may not be as a result of simple mineral dissolution and precipitation. Simple mineral dissolution can be ruled out because sodium carbonate minerals rarely occur (Mayo and Koontz, 2000) and are unlikely to exist in the bedrock lit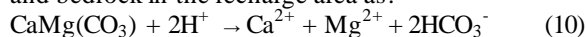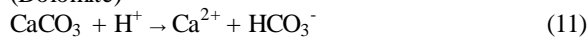hology in the study area. The solute composition of these waters may be the result of a series of interrelated and cascading chemical reactions. That is, CO$_2$ acquired from the soil zone or from other sources react with groundwater according to:

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (8)$$
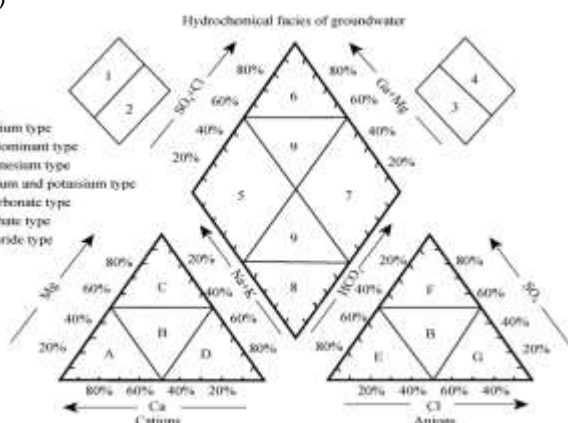$$H_2CO_3 \rightarrow HCO_3^- + H^+ \qquad (9)$$
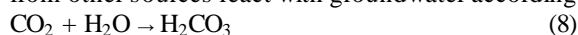
The groundwater then approached or attained carbonate mineral saturation by dissolving dolomite and calcite in the soil and bedrock in the recharge area as:

$$CaMg(CO_3) + 2H^+ \rightarrow Ca^{2+} + Mg^{2+} + 2HCO_3^- \qquad (10)$$
(Dolomite)
$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_3^- \qquad (11)$$
(Calcite)

Figure 6: Classification diagram for anion and cation facies in the form of major-ion percentages.

HCO$_3^-$ and Na$^+$- dominant water normally indicates ion-exchanged waters, although the generation of CO$_2$ at depth can produce HCO$_3^-$ where Na$^+$ is dominant under certain circumstances (Winograd and Farlekas, 1974). Garrels and Mackenzie (1967) pointed out that meteoric water dissolving Na from Na-bearing silicates would produce NaHCO$_3$ water type. Therefore, albite dissolution would have also probably produced NaHCO$_3$ water type.

A few of the boreholes (section II) also show Na–Cl water type suggesting end-product water.

It could be seen from Table 1 that the groundwaters have generally low salinity that range from 0.1 to 1.5‰. Mcneil et al. (2004) pointed out that low-salinity sodium-dominated water, but with roughly equal amounts of chloride and bicarbonate is characteristic of steep, high rainfall terrain and it also associated with feldspar weathering which can release sodium and potassium.

It is possible this process is happening in the Manya Krobo area where most of the boreholes are located in valleys of water courses.

Water types are designed according to the domains in which they occur on the diagram segments.
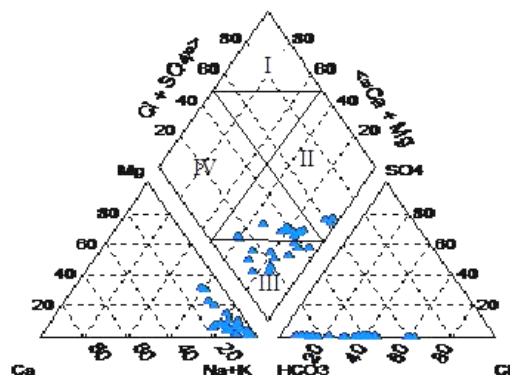
**Figure 7: Piper diagram showing groundwater samples from Manya Krobo area**

Mechanisms controlling groundwater chemistry

To know the groundwater chemistry and relationship of the chemical components of water from their respective aquifers such as chemistry of the rock types, chemistry of precipitated water and rate of evaporation, Gibbs (1970) has suggested a diagram in which ratio of dominant cations are plotted against the values of total dissolved solids (TDS). Gibbs diagrams, representing the ratio for cations [(Na+K)/(Na+K+Ca)] as a function of TDS is widely employed to assess the functional sources of dissolved chemical constituents, such as precipitation-dominance, rock-dominance and evaporation-dominance. The chemical data of groundwater samples are plotted in Gibbs diagram (Figure 8) and it was found that all of the samples suggested the chemical weathering of rock-forming minerals influencing the groundwater quality by means of dissolution of rocks through which water is circulating.
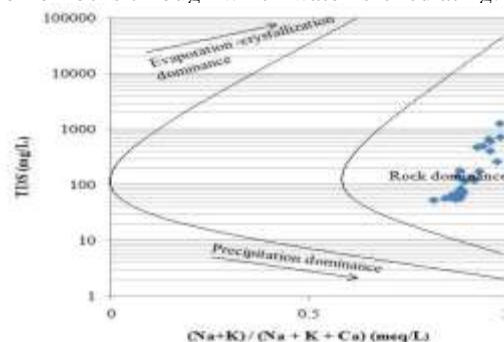
Figure 8: Gibbs variation diagram: TDS vs. (Na+K)/(Na+K+Ca)

Figure 9 is a plot of Cl$^-$ against Na$^+$; it can be observed that all of the samples plotted below the 1:1 line indicating excess of Na$^+$ over Cl$^-$. Excess Na$^+$ can be derived from sources that include plagioclase (albite) dissolution as per equation:

$$2NaAlSi_3O_8 + 2CO_2 + 11H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ 2HCO_3^- + 4H_4SiO_4 \qquad (12)$$
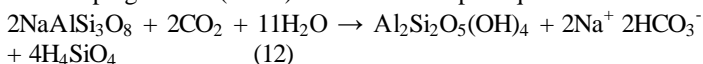
or cation exchange activity as shown by equation:

$$\frac{1}{2}Ca^{2+} + Na\text{-}clay \rightarrow \frac{1}{2}Ca\text{-}clay + Na^+ \qquad (13)$$
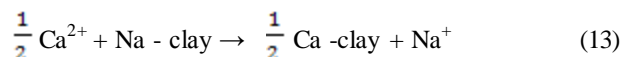
In order to investigate the occurrence of cation exchange reaction in the groundwater, Ca^{2+} + Mg^{2+} – (HCO$_3^-$ + SO$_4^{2-}$) (meq) was plotted against Na$^+$ + K$^+$ – Cl$^-$ (meq) (Figure 10).

Since calcite and dolomite are most likely additional sources that Ca^{2+} and Mg^{2+} could enter the groundwater apart from cation exchange, in plotting this diagram, possible contributions of Ca^{2+} and Mg^{2+} from calcite and dolomite dissolution to lithogenic Ca^{2+} and Mg^{2+} in the groundwater were

accounted for by subtracting the equivalent concentrations of HCO_3^- and SO_4^{2-} (McLean and Jankowski, 2000).

Similarly, to account for lithogenic Na^+ available for exchange, it was assumed that Na^+ contribution from meteoric origin would be balanced by equivalent concentration of Cl^- and, therefore, equivalent Cl^- concentration was subtracted from that of $Na + K$ (Nkotagu, 1996; McLean and Jankowski, 2000). The samples cluster around a line of slope -0.79, which can be approximated to equal -1. Water undergoing ion exchange plots along a line with a slope of -1 in $Ca^{2+} + Mg^{2+} - (HCO_3^- + SO_4^{2-})$ plot field (Jankowski et al., 1998). Thus, ion exchange is a significant process through which Na^+ partly enters the groundwater system.

Figure 9: A plot of Cl- against Na+(meq/L)

Figure 10: Bivariate plots of $Ca^{2+} + Mg^{2+} - (HCO_3^- + SO_4^{2+})$ versus $Na^+ + K^+ - Cl^-$

Suitability of groundwater for irrigation

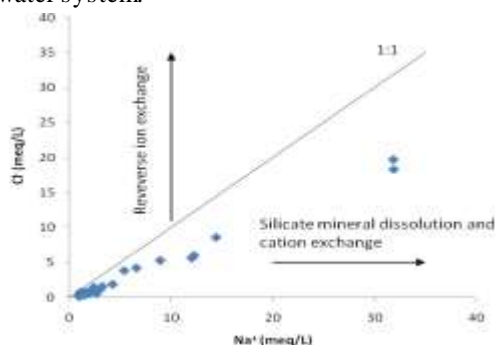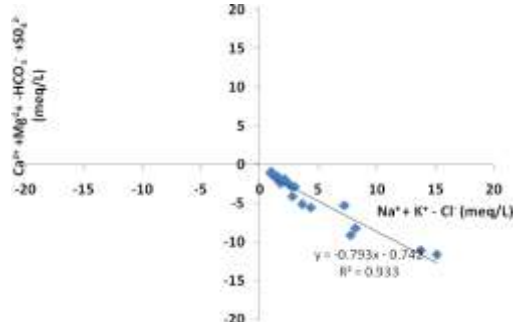Water quality, soil types and cropping practices play an important role for a suitable irrigation practice. Excessive amounts of dissolved ions in irrigation water affect plants and agricultural soil, both physically and chemically, thus reducing the productivity. The physical effects of these ions are to lower the osmotic pressure in the plant structural cells, thus preventing water from reaching the branches and leaves. The chemical effects disrupt plant metabolism. Water quality problems in irrigation include indices for salinity, chlorinity, sodicity (Mills, 2003) and alkalinity.

The important chemical constituents that affect the suitability of water for irrigation (Table 5) can be utilized to verify the suitability, as described as follows:

Salinity index or salinity hazard or total concentration of soluble/dissolved salt as computed in terms of measured Electrical Conductivity (EC) values; Sodicity index or sodium hazard or relative proportion of sodium to other principal cations as expressed by Sodium Absorption Ratio (SAR); Sodium hazard expressed as percent sodium of total cations (Na, %); Bicarbonate hazard or bicarbonate (HCO_3) concentrations as related to the concentration of calcium plus magnesium such as Residual Sodium Bicarbonate (RSBC); Chlorinity index (measured chloride ion concentrations in water); Magnesium

Hazard/Ratio (MH), Kelley Index (KI), Permeability Index (PI), Potential Salinity (PS), Soluble Sodium Percentage (SSP) and index of Base Exchange, Exchangeable Sodium Ratio (ESR).

Salinity index

Based on the analyses, the ground water samples have been classified as various classes (Handa, 1969), as given in Table 6.

It was found that all the samples collected were categorized under low to very high salinity classes. A good number of groundwater samples (44%) belong to low salinity category indicating that the water is of excellent quality.

Salinity index of the groundwater samples was computed using the measured electrical conductivity values. Water exhibiting low to moderate salinity is not considered very harmful to soils or crops, whereas, that exhibiting high salinity is suitable for irrigating the medium and high salt tolerant crops. High salinity water is suitable for irrigating high salt tolerant crops, whereas, water of very high salinity or above is generally unsuitable for irrigation.

Chlorinity index

Low salt tolerance crops are usually chloride sensitive. The chlorinity index of the groundwater sources was calculated using the measured chloride ion concentrations in water. Majority of the groundwater samples (92%) are found to be suitable (below 350mg/L) for irrigation.

Total hardness (TH)

In determining the suitability of groundwater for domestic and industrial purposes, hardness is an important criterion as it is involved in making the water become hard. Water hardness has no known adverse effects; however, it causes more consumption of detergents at the time of cleaning and some evidence indicates its role in heart disease (Schroeder, 1960). The Total Hardness (TH) (Todd, 1980; Hem, 1985; Ragunath, 1987) was determined by the following equation:

$$TH = 2.497 \ Ca^{2+} + 4.115 \ Mg^{2+} \qquad (14)$$

where Ca^{2+} and Mg^{2+} concentrations are expressed in meq/L.

The classification of groundwater in the study area based on hardness (Sawyer and McCarty, 1967) is presented in Table 7. Accordingly, all the samples (100%) collected fall under soft class.

Sodium Absorption Ratio (SAR) or sodicity index

Another important factor for water quality is the sodium concentration to express reactions with the soil and known reduction in its permeability. Because high sodium depositing waters are generally not suitable for irrigating the soils as higher deposition of sodium may deteriorate the soil characteristics. Therefore, Sodium Absorption Ratio (SAR) is considered as a better measure of sodium (alkali) hazard in irrigation water as it is directly related to the adsorption of sodium on soil and is a valuable criterion for determining the suitability of the water for irrigation. Excessive sodium contents relative to the calcium and magnesium reduce the soil permeability and thus inhibit the supply of water needed for the crops. The SAR measures the relative proportion of sodium ions in a water sample to those of calcium and magnesium. The SAR is used to predict the sodium hazard of high carbonate waters especially if they contain no residual alkali. The excess sodium or limited calcium and magnesium are evaluated by SAR (Kalra and Maynard, 1991) which is computed as:

$$SAR = \frac{Na^+}{\sqrt{\dfrac{Ca^{2+} + Mg^{2+}}{2}}} \qquad (15)$$

where all cationic concentrations are expressed in or meq/L.

The classification of groundwater samples from the study area with respect to SAR (Todd, 1959) is presented in Table 8. The SAR values of 76% of the samples are found to be less than 10, and are classified as being excellent for irrigation (i.e., S1 category).

Salinity hazard

For the purpose of diagnosis and classification, the total concentrations of soluble salts (salinity hazard) in irrigation water can be expressed in terms of specific conductance. Classification of groundwater based on salinity hazard (viz., electrical conductivity) is presented in Table 9.

It was found that only one sample was considered unsuitable for irrigation purposes. A more detailed analysis of the suitability of water for irrigation can be made by plotting sodium-absorption ratio and electrical conductivity (Figure 10) data on US Salinity Laboratory diagram (USSL, 1954). Accordingly, 11 samples (44%) fall in the category of the C1S1, indicating low salinity/low sodium type.

Of the remaining 14 samples, 6 samples belong to C2S1, indicating medium salinity/low sodium type, while 2 each samples belong to C3S1 and C3S2, illustrating high salinity/low sodium type and high salinity/medium sodium type, respectively. Also, 1 each of samples belong to C2S3, C3S4 and C4S4, meaning medium salinity/high sodium type, high salinity/very high sodium type and very high salinity/very high sodium type, respectively.

Groundwater samples that fall in the low salinity hazard class (C1) can be used for irrigation of most crops and in majority of soils. However, some leaching is required, but this occurs under normal irrigation practices except in soils of extremely low permeability. Groundwater samples that fall in medium salinity hazard class (C2) can be used if a moderate amount of leaching occurs.
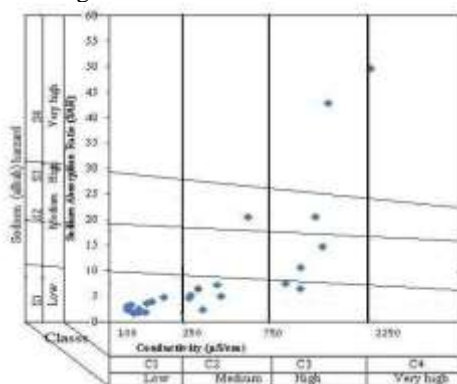

Figure 11. US salinity hazard diagram of water samples (after Richards, 1954)

High salinity/low sodium water (C4 and C5) can be suitable for plants with good salt tolerance but can restrict its suitability for irrigation, especially in soils with restricted drainage (Karanth, 1989; Mohan et al., 2000). High salinity water (C3, C4, and C5) cannot be used for irrigation of soils with restricted drainage. Even with adequate drainage, special management for salinity control is required and crops with good salt tolerance should be selected. Such areas need special attention as far as irrigation is concerned.

Percent sodium (Na %)

Methods of Wilcox (1995) and Richards (1954) have been used to classify and understand the basic characteristics of the chemical composition of groundwater since the suitability of the groundwater for irrigation depends on the mineralization of

water and its effect on plants and soil. Percent sodium can be determined using the following formula:

$$Na\% = \frac{Na^+}{(Na^+ + K^+ + Ca^{2+} + Mg^{2+})} \times 100 \qquad (16)$$

where the quantities of Ca^{2+}, Mg^{2+} Na^+ and K^+ are expressed in milliequivalents per litre (meq/L).

When the concentrations of sodium are high in irrigation water, sodium ions tend to be absorbed by clay particles, displacing Mg^{2+} and Ca^{2+} ions. This exchange process of Na^+ in water for Ca^{2+} and Mg^{2+} in soil would reduce the permeability and eventually give rise to soil with poor internal drainage. Hence, air and water circulation is restricted under wet conditions and such soils will become usually hard when dry (Saleh et al., 1999).

The classification of groundwater samples with respect to percent sodium is given in Table 10 and it was found that 7 samples belong to the good to permissible category. Based on Eaton's (1950) classification, 24 samples (96%) belong to the safe category (Table 5.11). Wilcox (1948) classified groundwater for irrigation purposes by correlating percent sodium (i.e., sodium in irrigation waters) and electrical conductivity.

A perusal of Wilcox's (1995) diagram (Figure 12) shows that of 25 samples, 17 (68%) belong to excellent to good, 2 samples (8%) to good to permissible, 1 sample (4%) to doubtful to unsuitable, 4 samples (16%) to permissible to doubtful and 1 samples (4%) to unsuitable category.

Figure 12: A plot of percentage of sodium vs. conductivity (after Wilcox, 1995).

Soluble sodium percentage (SSP)

Water quality for agricultural purposes in the Manya Krobo area shows that majority (52%) of the samples belong to unsuitable category based on Todd's classification of soluble sodium percentage (SSP) values, which is define as:

$$SSP = \left[\frac{Na^+}{(Na^+ + Ca^{2+} + Mg^{2+})} \right] \times 100 \qquad (17)$$

where all concentrations are expressed in meq/L.
SSP values range from 52.0 to 97.4 (Table 12).

The classification of groundwater in the study area based on hardness (Sawyer and McCarty, 1967) is presented in Table 7. Accordingly, all the samples (100%) collected fall under soft class.

Sodium Absorption Ratio (SAR) or sodicity index

Another important factor for water quality is the sodium concentration to express reactions with the soil and known reduction in its permeability. Because high sodium depositing waters are generally not suitable for irrigating the soils as higher deposition of sodium may deteriorate the soil characteristics. Therefore, Sodium Absorption Ratio (SAR) is considered as a better measure of sodium (alkali) hazard in irrigation water as it

is directly related to the adsorption of sodium on soil and is a valuable criterion for determining the suitability of the water for irrigation. Excessive sodium contents relative to the calcium and magnesium reduce the soil permeability and thus inhibit the supply of water needed for the crops. The SAR measures the relative proportion of sodium ions in a water sample to those of calcium and magnesium. The SAR is used to predict the sodium hazard of high carbonate waters especially if they contain no residual alkali. The excess sodium or limited calcium and magnesium are evaluated by SAR (Kalra and Maynard, 1991) which is computed as:

$$SAR = \frac{Na^+}{\sqrt{\dfrac{Ca^{2+} + Mg^{2+}}{2}}} \qquad (15)$$

where all cationic concentrations are expressed in or meq/L.

The classification of groundwater samples from the study area with respect to SAR (Todd, 1959) is presented in Table 8. The SAR values of 76% of the samples are found to be less than 10, and are classified as being excellent for irrigation (i.e., S1 category).

Salinity hazard

For the purpose of diagnosis and classification, the total concentrations of soluble salts (salinity hazard) in irrigation water can be expressed in terms of specific conductance. Classification of groundwater based on salinity hazard (viz., electrical conductivity) is presented in Table 9.

It was found that only one sample was considered unsuitable for irrigation purposes. A more detailed analysis of the suitability of water for irrigation can be made by plotting sodium-absorption ratio and electrical conductivity (Figure 10) data on US Salinity Laboratory diagram (USSL, 1954). Accordingly, 11 samples (44%) fall in the category of the C1S1, indicating low salinity/low sodium type.

Of the remaining 14 samples, 6 samples belong to C2S1, indicating medium salinity/low sodium type, while 2 each samples belong to C3S1 and C3S2, illustrating high salinity/low sodium type and high salinity/medium sodium type, respectively. Also, 1 each of samples belong to C2S3, C3S4 and C4S4, meaning medium salinity/high sodium type, high salinity/very high sodium type and very high salinity/very high sodium type, respectively.

Groundwater samples that fall in the low salinity hazard class (C1) can be used for irrigation of most crops and in majority of soils. However, some leaching is required, but this occurs under normal irrigation practices except in soils of extremely low permeability. Groundwater samples that fall in medium salinity hazard class (C2) can be used if a moderate amount of leaching occurs.

Figure 11. US salinity hazard diagram of water samples (after Richards, 1954)

High salinity/low sodium water (C4 and C5) can be suitable for plants with good salt tolerance but can restrict its suitability for irrigation, especially in soils with restricted drainage (Karanth, 1989; Mohan et al., 2000). High salinity water (C3, C4, and C5) cannot be used for irrigation of soils with restricted drainage. Even with adequate drainage, special management for salinity control is required and crops with good salt tolerance should be selected. Such areas need special attention as far as irrigation is concerned.

Percent sodium (Na %)

Methods of Wilcox (1995) and Richards (1954) have been used to classify and understand the basic characteristics of the chemical composition of groundwater since the suitability of the groundwater for irrigation depends on the mineralization of water and its effect on plants and soil. Percent sodium can be determined using the following formula:

$$Na\% = \frac{Na^+}{(Na^+ + K^+ + Ca^{2+} + Mg^{2+})} \times 100 \qquad (16)$$

where the quantities of Ca^{2+}, Mg^{2+} Na^+ and K^+ are expressed in milliequivalents per litre (meq/L).

When the concentrations of sodium are high in irrigation water, sodium ions tend to be absorbed by clay particles, displacing Mg^{2+} and Ca^{2+} ions. This exchange process of Na^+ in water for Ca^{2+} and Mg^{2+} in soil would reduce the permeability and eventually give rise to soil with poor internal drainage. Hence, air and water circulation is restricted under wet conditions and such soils will become usually hard when dry (Saleh et al., 1999).

The classification of groundwater samples with respect to percent sodium is given in Table 10 and it was found that 7 samples belong to the good to permissible category. Based on Eaton's (1950) classification, 24 samples (96%) belong to the safe category (Table 5.11). Wilcox (1948) classified groundwater for irrigation purposes by correlating percent sodium (i.e., sodium in irrigation waters) and electrical conductivity.

A perusal of Wilcox's (1995) diagram (Figure 12) shows that of 25 samples, 17 (68%) belong to excellent to good, 2 samples (8%) to good to permissible, 1 sample (4%) to doubtful to unsuitable, 4 samples (16%) to permissible to doubtful and 1 samples (4%) to unsuitable category.
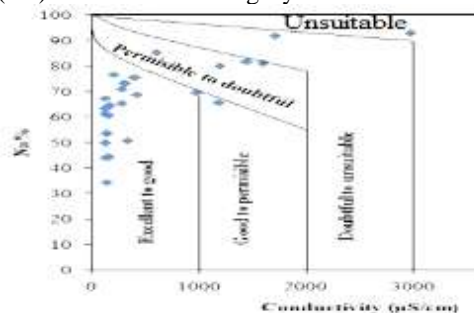

Figure 12: A plot of percentage of sodium vs. conductivity (after Wilcox, 1995).

Soluble sodium percentage (SSP)

Water quality for agricultural purposes in the Manya Krobo area shows that majority (52%) of the samples belong to unsuitable category based on Todd's classification of soluble sodium percentage (SSP) values, which is define as:

$$SSP = \left[\frac{Na^+}{(Na^+ + Ca^{2+} + Mg^{2+})}\right] \times 100 \qquad (17)$$

where all concentrations are expressed in meq/L.

SSP values range from 52.0 to 97.4 (Table 12).

Residual sodium carbonate (RSC)

In addition to the SAR and (Na, %), the excess sum of carbonate and bicarbonate in groundwater over the sum of calcium and magnesium also influences the suitability of groundwater for irrigation. Because, in waters having high concentrations of bicarbonate, there is a tendency for calcium and magnesium to precipitate as the water in the soil becomes more concentrated. An excess quantity of sodium bicarbonate and carbonate is considered to be detrimental to the physical properties of soils as it causes dissolution of organic matter in the soil, which in turn leaves a black stain on the soil surface on drying. As a result, the relative proportion of sodium in the water is increased in the form of sodium carbonate and this excess is denoted by Residual Sodium Carbonate (RSC) is calculated as follows (Eaton, 1950; Ragunath, 1987):

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \qquad (18)$$

where all ionic concentrations are expressed in meq/L.

According to the US Department of Agriculture, water with more than 2.50 meq/L of RSC is not suitable for irrigation purposes. Groundwater samples were classified on the basis of RSC and it was found that 8 samples (44%) belong to the doubtful category, while 8 samples (32%) have RSC values above 2.50mg/L and only 6 samples (24%) showed RSC values less than 1.25 meq/L. All positive RSC values indicate that dissolved Ca^{2+} and Mg^{2+} ions were less than CO_3^{2-} and HCO_3^- contents (Table 13).

Residual sodium bicarbonate (RSBC)

Gupta and Gupta (1987) defined RSBC (Residual Sodium Bicarbonate) as given in equation (4)

$$RSBC = (HCO_3^- - Ca^{2+}) \qquad (19)$$

The RSBC values varied from 0.88 to 11.09 meq/L and 18 samples (72%) collected were found to be satisfactory (<5 mg/L) according to the criteria set by Gupta and Gupta (1987).

Permeability index (PI)

The Permeability Index (PI) values also indicate the suitability of groundwater for irrigation, as the soil permeability is affected by long-term use of irrigation water, as influenced by Na^+, Ca^{2+}, Mg^{2+} and HCO_3^- contents of the soil. Doneen (1964) and Ragunath (1987) evolved a criterion for assessing the suitability of water for irrigation based on a Permeability Index (PI) and waters can be classified as Class I, Class II, and Class III. Permeability Index (PI) can be written as follows:

$$PI = \frac{(Na^+ + \sqrt{HCO_3})}{(Ca^{2+} + Mg^{2+} + Na^+ + K^+)} \times 100 \qquad (20)$$

where the concentrations are reported in meq/L.

The permeability index (Table 5) of the Manya Krobo area ranged from 17.15% to 77.14% during post monsoon season of September 2009. It was found that all the samples categorized under classes I and II of Doneen's chart (Domenico and Schwartz, 1990; WHO, 1989) (Figure 13).

Potential Salinity (PS)

Doneen (1954, 1962) pointed out that the suitability of water for irrigation is not dependent on the concentrations of soluble salts. Doneen (1962) is of the opinion that the low soluble salts gets precipitated in the soil and accumulated with each successive irrigation, whereas the concentrations of highly soluble salts enhance the salinity of the soil. Potential salinity is defined as the chloride concentration plus half of the sulfate concentration:

$$Potential \ Salinity = Cl^- - \frac{1}{2}SO_4^{2-} \ (meq \ / \ L) \qquad (21)$$

The PS values are more pronounced in samples from boreholes near the Volta Lake than those farther from the Volta Lake. The high potential salinity in the proximity of the lake is due to the presence of chlorides, which are derived from rock source. The potential salinity of the water samples varied from 0.1 to 19.7.

Ion-exchange processes

Control on the dissolution of undesirable constituents in water is impossible during the subsurface runoff, but it is essential to know various changes in chemical composition undergone by groundwater during their trend/travel in the sub-surface (Johnson 1979; Sastri, 1994). The chloro-alkaline indices CAI-1 and CAI-2 are suggested by Schoeller (1965, 1967, 1977), which indicates ion exchange between the groundwater and its host environment during residence or travel. If there are Na^+ and K^+ ions in water which are exchanged with Mg^{2+} and Ca^{2+} ions, the indices are positive, indicating direct base Exchange reaction or chloro-alkaline equilibrium.

In contrast, if the exchange is in the reverse order, then the exchange is indirect and the indices are found to be negative, indicating chloro-alkaline disequilibrium.
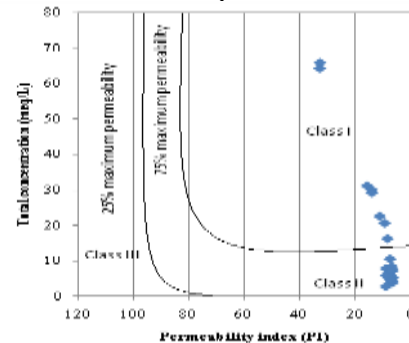
Figure 13: Doneen chart of permeability index for the Manya Krobo area

These reactions are known as cation–anion exchange reactions viz., ion exchange between the groundwater and its host environment during residence or travel in the sub-surface. The chloro-alkaline indices used in the evaluation of Base Exchange are calculated using the following formulae:

$$Chloro\text{-}alkaline \ index \ 1 = \frac{Cl-(Na+K)}{Cl} \qquad (22)$$

$$Chloro\text{-}alkaline \ index \ 2 = \frac{Cl-(Na+K)}{(SO_4+HCO_3+NO_3)} \qquad (23)$$

It was found from the chloro-alkaline indices calculated for samples that all the samples from the Manya Krobo area showed negative ratios indicating an indirect base-exchange reaction. During this process, the host rocks are not considered to be the primary sources of dissolved solids in the water.

Schoeller indices of the groundwater samples revealed that cation–anion exchange (chloro-alkaline disequilibrium) exist all over the area. Groundwater with a base-exchange reaction in which the alkaline earths have been exchanged for Na^+ ions ($HCO_3^- > Ca^{2+}+Mg^{2+}$) may be referred to as base-exchange-softened water, and that in which the Na+ ions have been exchanged for the alkaline earths ($Ca^{2+}+ Mg^{2+} > HCO_3^-$) may be referred to as base-exchange hardened water (Handa, 1979). In the study area, all the samples had higher HCO_3^- concentrations over alkaline earths, indicating the base exchange-softened water nature.

Magnesium hazard (MH)

Generally, calcium and magnesium maintain a state of equilibrium in most waters. Calcium and magnesium do not behave equally in the soil system and magnesium deteriorates soil structure particularly when waters are sodium-dominated and highly saline. High level of Mg^{2+} is usually due to the presence of exchangeable Na^+ in irrigated soils. In equilibrium, more Mg^{2+} present in water will adversely affect the soil quality rendering it alkaline, resulting in decreased and adversely affected crop yields. Paliwal (1972) introduced an important ratio called index of magnesium hazard. Magnesium index of more than 50% would adversely affect the crop yield as the soils become more alkaline.

$$\text{Magnesium hazard (MH)} = \frac{Mg^{2+} \times 100}{(Mg^{2+} + Ca^{2+})} \qquad (24)$$

In the Manya Krobo area, the magnesium hazard (MH) values were reported to be in the range of 14.61% to 77.96%. Of the 25 samples, 56% of the samples showed magnesium index value below 50%, suggesting their suitability, while 44% fall in the unsuitable category with MH more than 50%, indicating their adverse effect on crop yield.

Magnesium ratio (MR)

Based on the Mg/Ca ratio, waters can be classified as suitable or unsuitable for irrigation. Accordingly, 92% of the samples belong to the safe to moderate categories (Table 15).

Exchangeable sodium ratio (ESR)

Exchangeable sodium ratio (ESR) can be defined as:

$$ESR = \frac{Na^+}{(Mg^{2+} + Ca^{2+})} \qquad (25)$$

Water quality for agricultural purposes in the study area based on ESR values varied from 1.09 to 38.53.

Origin of recharge

The $\delta^{18}O$ values of the groundwater samples vary from -3.61 to -2.17‰ vs. VSMOW with a mean and standard deviation of –2.91‰ vs. VSMOW and 0.37 respectively. The δ^2H values range from -15.63 to -7.92‰ vs. VSMOW with mean and standard deviation of -11.18‰ vs. VSMOW and 1.73 respectively. A plot of δ^2H against $\delta^{18}O$ of the analyzed samples is shown in Figure14. Two meteoric water lines were inserted. These include that obtained by Craig (1961):
$\delta^2H = 8\delta^{18}O + 10$, i.e, Global Meteoric Water Line (GMWL);
And that obtained by Akiti (1980):   (26)
$\delta^2H = 7.86\delta^{18}O + 13.6$, i.e, a Local Meteoric Water Line (LMWL).
GMWL, $\delta^2H = 8\delta^{18}O + 10$ (Craig 1961)   (27)

Majority of the groundwater samples cluster around the meteoric water line (fig. 14) indicating that groundwater was recharged predominantly from rainfall. However, some the recharging water might have undergone some evaporation in the atmosphere or in the soil zone before reaching the groundwater table. The isotopically depleted samples were those away from the Volta lake (on the Kwahu Plateau) whilst enriched groundwater samples were those in the proximity of the Volta Lake where Kaka, 2010 identified possible infiltration of lake water into aquifers at the lake shores.

Conclusion

The groundwater resources in the Manya Krobo area were evaluated for their chemical composition and suitability for drinking and irrigation. The physico-chemical parameters like hardness, nitrates, sulphates, calcium of most of the groundwater

samples analyzed in the present investigation were generally low. The groundwater in the area is classified as soft based on hardness, while RSC values specify that water samples belong to good to unsuitable classes. Permeability index recommends that the water samples from the Manya Krobo area are suitable for irrigation. All the samples had negative chloro-alkaline indices, illustrating that they had chloro-alkaline disequilibrium. The suitability of groundwater for irrigation was evaluated based on the irrigation quality parameters, revealing that the majority of the samples fall in excellent to suitable categories for irrigation. From U.S. Salinity hazard diagram, it is evident that about 44% of the samples are grouped within C1S1 classes, indicating low salinity and low sodium type. From Wilcox plot, it is observed that most of the samples from the study area fall in the excellent to good classes for irrigation purpose. The samples which are not suitable based on the irrigation quality parameters may be suitable in well-drained soils. Based on the attempt made to study the hydrochemistry of groundwater, it was found that HCO_3 type dominated the anions and Na-K type dominated the cations during the post monsoon period of September 2009. The water type that predominates in the study area is of Na–K–HCO_3-Cl (48%) type, followed by Na–HCO_3 (40%) and Na–Cl (12%) types. It was also noticed that alkali elements exceeded alkaline earth metals concentrations and weak acids exceeded the strong acid ions. Based on Cl, SO_4, HCO_3 concentrations, the groundwater sources were categorized as normal chloride (92%) and normal sulphate (100%) and normal bicarbonate (56%) types.
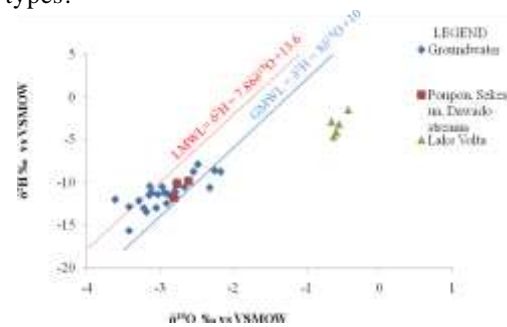
Figure 14: A graph of delta deuterium against delta oxygen-18 of water samples

Analysis of stable isotope ratios of hydrogen and oxygen (δ^2H and $\delta^{18}O$) of the groundwater samples suggests that the aquifers receive rapid and recharge mainly from rainfall.

Further, Gibbs plot indicated that the chemistry of groundwater of the area is predominantly controlled by rock dominance i.e., an interaction exists between the litho units and the percolating water into the subsurface. Finally, it can be concluded that the overall quality of groundwater is controlled by lithology.

Acknowledgements

References

Acheampong, S.Y., Hess, J.W. (1998). Hydrogeologic and hydrochemical framework of the shallow groundwater system in the southern Voltaian Sedimentary Basin, Ghana. *Journal of Hydrogeology* 6: 527–537.

Acheampong, S.Y., Hess, J.W. (2000). Origin of the shallow groundwater system in the southern Voltaian Sedimentary Basin of Ghana: an isotopic approach. *Journal of Hydrology* 233:37-53.

Adomako, D.; Osae, S.;Akiti, T. T.; Faye, S.; Maloszewski, P. Geochemical and isotopic studies of groundwater conditions in the Densu River Basin of Ghana. *Environ Earth Sci*. DOI 10.1007/s12665-010-0595-2

Affaton, P., Sougy, J., Trompette, R. (1980). The tectono-stratigraphic relationships between the Upper Precambrian and Lower Paleozoic Volta basin and the Pan African Dahomeyide orogenic belt (West Africa). Am. J. Sci. 280, 224–248

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.*

Akiti, T.T. (1980). Etude Geochemique et Isotope de quelque aquifers du Ghana. These Dr. Ing. Univ. de Paris.

Ako, J.A., Wellman, P. (1985). The margin of the West African craton: the Voltaian Basin. J. Geol. Soc. London 142, 625–626.

Anani, C. (1999). Sandstone petrology and provenance of the Neoproterozoic Voltaian Group in the southeastern Voltaian Basin, Ghana. *Sedimentary Geology* 128: 83–98

Babiker I.S., Mohamed M.A.A., and Hiyama T. (2007). Assessing groundwater quality using GIS. *Water Resour. Manage.* 21, 699–715.

Cahen, L., Snelling, N.J., Delhal, J., Vail, J.R. (1984). The Geochronology and Evolution of Africa. Clarendon Press, Oxford, pp. 363–371

Craig, H. (1961). Standard for reporting concentrations of deuterium and oxygen-18 in natural waters. Science 133, 1833-1834.

Dapaah-Siakwan, S., Gyau-Boakye, P. (2008). Hydrogeologic framework and borehole yields in Ghana. *Hydrogeology Journal* 8:405–416.

Davis, S.N., De Wiest, R.G.M. (1966). Hydrogeology New York. Willey, London, p 463.

Domenico P.A. and Schwartz F.W. (1990). *Physical and Chemical Hydrogeology*. pp.410 420. Wiley, New York.

Doneen L.D. (1954). Salination of soil by salts in the irrigation water. *American Geophysical Union Transactions.* 35, 943–950.

Doneen L.D. (1962). The influence of crop and soil on percolating water. pp.156–163. In *Proceedings of the Biennial Conference on Ground Water Recharge*.

Doneen L.D. (1964). Notes on water quality in agriculture. In *Water Science and Engineering Paper 4001*. Dept. of Water, Science and Engineering, Univ. of California, Davis, USA.

Eaton E.M. (1950). Significance of carbonate in irrigation water. *Soil Sci.* 69, 12–133.

Edmunds W.M., Carillo-Rivera J.J., and Cardona A. (2002). Geochemical evolution of groundwater beneath Mexico City. *J Hydrol.* 258, 1–24.

Escolero, O., Marin, L.E., Steinch, B., Pacheco, J.A., Molina-Maldonado, A., Anzaldo, J.M. (2005). *Geochemistry of the hydrogeological reserve of Me´rida, Yucatan, Mexico. Geofisica Internacional* 44 (3): 301–314.

Farnham, I.M., Stetzenbach, K.J., Singh, A.K., Johannesson, K.H. (2002). Treatment of nondetects in multivariate analysis of groundwater geochemistry data. *Chemometrics and Intelligent Laboratory Systems* 60, 265–281.

Garrels, R. M., Mackenzie, F.T. (1967). Origin of the chemical compositions of some springs and lakes. In: Stumm W

(Chairman) Proc Symp Equilibrium Concepts in Natural Water Systems, Advances in Chem Ser 67, American Chemical Society,Washington, DC, pp 222–242.

Garrels, R.M., Mackenzie, F.T. (1967). Origin of the chemical composition of some springs and lakes. In: Stumm, W. (Ed.), Equilibrium Concepts in Natural Water Systems: Advances in Chemistry Series No. 67. American Chemical Society, Washington, DC, pp. 222–242.

Gibrilla A.; Osae S.; Akiti T. T.; Adomako D.; Ganyaglo S.Y., Bam E. P. K.; Hadisu A. (2010). Origin of Dissolve Ions in Groundwaters in the Northern Densu River Basin of Ghana Using Stable Isotopes of ^{18}O and ^{2}H. *J. Water Resource and Protection,* 2, 1010-1019 doi:10.4236/jwarp.2010.212121

Handa B.K. (1979). Groundwater pollution in India. *In Proceedings of National Symposium on Hydrology*. pp. 34–49. IAHS, Publ. Univ. Roorkee, India.

Hem, J. D. (1985). Study and Interpretation of Chemical Characteristics of Natural Water, 3rd Ed. U.S. Geological Survay, Water Supply paper 2254.

IAEA, (2001). Use of research reactors for neutron activation analysis. Report of an Advisory Group meeting held in Vienna, 22–26 June 1998. IAEA-TECDOC-1215 ISSN 1011–4289

Jaganathan, V., Tamta, S. R., Srikantha, N. P. (1991). Behaviour of groundwater level and quality in Karnataka State during 1979–88. Central Ground Water Board, Ministry of Water Resources, Government of India, New Delhi. IAEA-TCS-35, 2009

Junner, N.R., Hirst, T. (1946). The geology and hydrogeology of the Volta Basin. Memoir 8, Gold Coast Geological Survey.

Junner, N.R., Service, H. (19360). Geological notes on Volta River District and Togoland under British mandate. Annual Report on the Geological Survey by the Director, 1935–1936.

Kaka, E.A. (2010). Hydrogeochemical and Isotopic study of groundwater along the Volta Lake: Manya Krobo area, Ghana. M.Phil thesis, University of Ghana, Legon.

Kalra Y.P. and Maynard D.G. (1991). Methods Manual for Forest Soil and Plant Analysis. In *Information Report NOR-X-319*. Northwest Region, Northern Forestry Centre, Forestry Canada.

Karath K.R. (1989). *Quality of Ground Water Assessment Development and Management*. pp.217–275. Tata McGraw-Hill, NewDelhi

Kortatsi, B. K. (1994). Groundwater utilization in Ghana. Paper presented in the Proceedings of the Helsinki Conference, June 1994. In: Future Groundwater Resources at Risk. IAHS Publ. no. 222, 149

Kortatsi, B.K. (2003). Acdification of Groundwater and its Implication on Rural Water Supply in the Ankobra Basin, Ghana. *West Africa Journal of Applied Ecology* Vol.4 pp 35-47

Kortatsi, B.K. (2006). Hydrochemical characterization of groundwater in the Accra plains of Ghana. *Environ Geol* 50: 299–311

Kortatsi, B.K., Anku, Y. S. A., Anornu, G. K. (2008). Characterization and appraisal of facets influencing geochemistry of groundwater in the Kulpawn sub-basin of the White Volta Basin, Ghana. *Environ Geol*. DOI 10.1007/s00254-008-1638-9

McNeil, V.H., Cox, M.E., Preda, M. (2005). Assessment of chemical water types and their spatial variation using multi-stage cluster analysis, Queensland, Australia. *Journal of Hydrology* 310:181–200

Mills B. (2003). *Interpreting Water Analysis for Crop and Pasture*. File No. FS0334, DPI's Ageny for Food and Fiber Sciences, Toowoomba.

Mohan R., Singh A.K., Tripathi J.K., et al. (2000). Hydrochemistry and quality assessment of ground water in Naini Industrial area, Allahabad district, Uttar Pradesh. *J. Geol. Soc. Ind.* 55, 77–89.

Nyarko, B.K ., Essumang, D. K; Eghan, M.J.; Reichert, B; van de Giesen, N; Vlek P (2010) . Use of isotopes to study floodplain wetland and river flow interaction in the White Volta River basin, Ghana. *Isotopes in Environmental and Health Studies.* 46, 91–106.

Paliwal K.V. (1967). Effect of gypsum application on the quality of Irrigation waters. *The Madras Agricultural Journal.* 59,646–647.

Paliwal K.V. (1972). *Irrigation With Saline Water* (p. 198) Monogram No. 2 (New series). New Delhi: IARI.

Pelig-Ba, K.B. (2009). Analysis of Stable Isotope Contents of Surface and Underground Water in Two Main Geological Formations in the Northern Region of Ghana. *West African Journal of Applied Ecology, vol.*15.

Petters, S.W. (1991.) Regional Geology of Africa. Lecture Notes in Earth Sciences 40, Springer, Berlin, pp. 296–302.

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

Ragunath H.M. (1987) *Groundwater.* pp.563. Wiley Eastern, New Delhi

Richards L.A. (U.S. Salinity Laboratory) (1954). *Diagnosis and Improvement of Saline and Alkaline Soils.* pp.60. U.S. Department of Agriculture Hand Book.

Saleh A., Al-Ruwaih F., and Shehata M. (1999). Hydrogeochemical processes operating within the main aquifers of Kuwait. *J. Arid Environ.* 42, 195–209.

Saunders, R.S., 1970. Early Paleozoic orogeny in Ghana: foreland stratigraphy and structure. Geol. Soc. Am. Bull. 81, 233–240.

Sawyer G.N. and McCarthy D.L. (1967). *Chemistry of Sanitary Engineers* (2nd ed.). pp.518. McGraw Hill, New York.

Schoeller H. (1965). Qualitative evaluation of groundwater resources. In *Methods and Techniques of Groundwater Investigations and Development*. pp.54–83. UNESCO.

Schoeller H. (1967). Geochemistry of groundwater. *In An International Guide for Research and Practice*. pp.1–18. UNESCO, Chap.15.

Schoeller H. (1977). Geochemistry of groundwater, Chap. 15. In *Groundwater Studies: An International Guide for Research and Practice* . pp.1–18. UNESCO, Paris.

Schroeder H.A. (1960). Relations between hardness of water and death rates from certain chronic and degenerative diseases in the United States . *J. Chron. Disease.* 12, 586–591.

Todd D.K. (1959). *Groundwater Hydrology.* pp.535. John Wiley & Sons.

Wilcox L.V. (1948). The quality water for irrigation use. *US Dept. Agric. Bull.* 1962, 40.

Wilcox L.V. (1995). *Classification and Use of Irrigation Waters.* pp.19. US Department of Agriculture, Washington DC.

Yidana, S.M. (2008). Yidana, S.M. (2010). Groundwater classification using multivariate statistical methods: Southern Ghana. Journal Groundwater resources management for productive uses in the Afram Plains area, Ghana. Doctoral Dissertation, Montclair State University, USA.

Yidana, S.M., Ophori, D., Banoeng-Yakubo, B. (2007). Groundwater availability in the shallow aquifers of the southern voltaian system: a simulation and chemical analysis. *Environmental Geology* 55:1647–1657.

Yidana, S.M., Ophori, D., Banoeng-Yakubo, B. (2007). Hydrochemical evaluation of the Voltaian system—The Afram Plains area, Ghana. *Journal of Environmental Management*, doi:10.1016/j.jenvman.2007.03.037.

Yidana, S.M., Ophori, D., Banoeng-Yakubo, B. (2008). Groundwater availability in the shallow aquifers of the southern Voltaian system: a simulation and chemical analysis. *Environmental Geology* 55: 1647–1657.

Yidana, S.M., Ophori, D., Banoeng-Yakubo, B. (2008). Groundwater quality evaluation for productive uses – the Afram Plains area, Ghana. *Journal of Irrigation and Drainage Engineering* 134 (2): 222–227.

Yidana, S.M., Ophori, D., Banoeng-Yakubo, B. (2008). Hydrochemical evaluation of the Voltaian system–the Afram Plains area, Ghana. *Environmental Management* 88: 697–707.

Yidana, S.M., Ophori, D., Banoeng-Yakubo, B. (2008). Hydrogeological and hydrochemical characterization of the Voltaian Basin: the Afram Plains area, Ghana. *Environmental Geology 53*: 1213–1223.

Table 1: Non-ionic parameters determined in groundwater samples

Location/Statistics	pH	Eh (mV)	Temp (^{0}C)	EC (µS/cm)	TDS (mg/L)	Salinity (‰)
Oborpa west	6.92	-33.5	27.3	2970.0	1274.0	1.5
Bweyonye	6.62	-12.7	29.0	1709.0	729.0	1.5
Oterkpolou	6.45	-1.7	27.8	335.0	142.2	0.1
Bormase Tenya-1	5.24	70.8	26.9	137.4	59.2	0.1
Bormase Tenya-2	6.21	14.1	26.6	146.1	65.9	0.1
Sekeswa	6.82	-21.8	27.1	125.3	53.8	0.1
Akatawia	6.67	-11.9	27.1	202.0	87.1	0.1
Abetima	6.65	-11.4	28.1	281.0	118.8	0.1
Ban Dawa	6.82	-22.4	26.8	604.0	265.0	0.3
Kasakope	6.80	-21.5	28.0	1590.0	673.0	0.7
Kponyokope	6.87	-24.4	28.2	1447.0	607.0	0.7
Apimsu-1	6.81	-19.1	26.2	316.0	137.3	0.1
Apimsu-2	6.74	-17.4	26.5	405.0	176.1	0.2
Seseaman sisi	6.48	-2.5	25.3	129.9	58.1	0.1
Seseaman kperti	6.37	4.7	25.6	132.1	58.7	0.1
Brepaw Kperti	6.39	2.9	25.7	125.7	55.7	0.1
Asesewa	6.51	-4.0	25.4	161.7	72.1	0.1
Akrusu sisi	6.76	-18.1	28.3	982.0	411.0	0.4
Aworworso	6.61	-8.8	27.8	158.9	67.1	0.1
Seseaman north	6.51	-3.7	26.6	172.9	75.2	0.1
Akotoe	6.83	-22.1	28.4	1196.0	504.0	0.6
Treboanya	6.85	-27.2	29.4	1190.0	483.0	0.5
Akrusu Yiti-1	6.71	-14.9	27.3	145.9	62.8	0.1
Akrusu Yiti-2	6.69	-13.7	27.2	286.0	122.7	0.1
Mensa Dawa	6.78	-19.3	26.5	425.0	183.0	0.2
Minimum	5.24	-33.5	25.3	125.3	53.8	0.1
Maximum	6.92	70.8	29.4	2970.0	1274.0	1.5
Mean	6.60	-9.6	27.2	615.0	261.7	0.3
Median	6.69	-13.7	27.1	286.0	122.7	0.1
Std. deviation	0.34	20.1	1.1	708.6	300.8	0.4

Table 2: Concentration of major ions in mg/L determined in the groundwater samples

Location/Statistics	ID	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	Cl$^-$	HCO$_3^-$	NO$_3^-$	SO$_4^{2-}$	ICB
Oborpa	MKI	733.00	61.00	11.57	3.02	649.80	712.00	0.04	1.44	6.6
Bweyonye	MK2	732.00	66.00	11.10	6.73	699.80	696.00	1.57	4.16	5.1
Oterkpolou	MK3	44.50	15.00	6.54	14.05	20.00	216.00	0.16	1.17	-4.2
Bormase Tenya-1	MK4	22.10	40.30	5.30	6.37	10.00	144.00	0.96	0.81	1.9
Bormase Tenya-2	MK5	34.70	19.30	5.24	6.74	14.00	130.00	1.61	0.98	4.6
Sekeswa	MK6	21.30	7.80	5.10	0.96	4.00	78.00	0.04	0.64	1.9
Akatawia	MK7	48.80	9.10	6.18	1.19	38.00	88.00	1.55	0.17	4.1
Abetima	MK8	54.60	27.70	7.36	2.08	52.00	136.00	0.00	1.11	-1.3
Ban Dawa	MK9	331.00	57.00	7.96	7.23	305.00	352.00	0.00	0.11	7.9
Kasakope	MK10	276.00	56.00	12.84	8.55	200.00	580.00	0.36	6.64	-1.7
Kponyokope	MK11	281.00	78.00	12.19	1.27	213.00	496.00	4.39	5.36	2.1
Apimsu-1	MK12	67.60	25.10	6.82	1.10	40.00	152.00	0.00	0.42	5.0
Apimsu-2	MK13	97.10	25.40	7.28	4.22	67.00	192.00	0.00	0.46	5.1
Seseaman sisi	MK14	23.80	22.80	6.00	1.91	23.00	72.00	1.34	0.13	5.7
Seseaman kperti	MK15	35.00	10.30	5.77	2.19	27.00	76.00	2.06	0.08	4.9
Brepaw Kperti	MK16	34.20	16.70	5.67	2.64	18.00	100.00	1.34	0.39	5.2
Asesewa	MK17	36.80	24.30	6.38	1.10	16.00	120.00	0.52	0.16	4.0
Akrusu sisi	MK18	123.20	50.00	5.74	9.26	136.00	292.00	0.00	1.37	-5.9
Aworworso	MK19	26.40	22.30	5.52	6.93	25.00	100.00	2.93	0.08	3.5
Seseaman north	MK20	43.90	21.60	6.04	2.37	26.00	144.00	1.14	0.73	-2.8
Akotoe	MK21	204.60	30.50	12.34	9.80	188.00	380.00	0.00	0.40	-1.9
Treboanya	MK22	150.70	50.70	12.72	18.04	150.00	396.00	0.00	0.44	-3.7
Akrusu Yiti-1	MK23	31.00	18.20	5.62	11.66	15.00	154.00	0.85	0.28	1.4
Akrusu Yiti-2	MK24	73.50	20.10	6.64	5.51	56.00	143.00	1.84	1.34	6.1
Mensa Dawa	MK25	60.60	24.10	8.82	1.66	20.00	178.00	0.02	0.51	4.6
Minimum		21.3	7.8	5.09	0.96	72	72	0	0.077	
Maximun		733	78	12.84	18.04	712	712	4.39	6.643	
Mean		143.5	32	7.71	5.46	245.1	121	0.91	1.175	
Median		54.6	24.3	6.53	4.22	152	193	0.52	0.511	
Standard dev.		198.2	19.6	2.69	4.52	193.8	185	1.1	1.681	

Note: MKI and MK2 are found in Buem formation; MK3 to MK6 are found in Kwahu Sandstone Member; and MK7 to MK25 are found in Anyoboni Sandstone Member.

Table 3: Characterization of groundwater of the Manya Krobo area based on Piper tri-linear diagram

Subdivision of the diamond	Characteristics of corresponding subdivisions of diamond-shaped field	No	%
1	Alkaline earth (Ca+Mg) exceeding alkalies (Na+K)	00	00
2	Alkalies exceeding alkaline earths	25	100
3	Weak acids (CO$_3$+HCO$_3$) exceeding strong acids (SO$_4$+Cl)	22	88
4	Strong acids exceeding weak acids	3	12
4	Magnesium bicarbonate type	00	00
5	Calcium-chloride type	00	00
6	Sodium-chloride type	03	12
7	Sodium-bicarbonate type	10	40
8	Mixed type (No cation-anion exceeding 50%)	12	48

Table 4: Variations in hydrochemical facies in the Manya Krobo area

Water type	Sample No.	Freq.	%
Na-HCO3-Cl	7, 8, 10, 11, 12, 13, 15, 16 ,18, 20, 21, 22, 24	13	52
Na-Cl-HCO3	1, 2, 9	3	12
Na-HCO3	5, 6, 25	3	12
Na-Mg-HCO3	3, 23	2	8
Na-K-HCO3-Cl	14	1	4
Mn-HCO3	17	1	4
Na-K-Mg-HCO3-Cl	19	1	4
K-Na-HCO3	4	1	4

Table 5: Irrigation water quality parameters for groundwater samples collected in the Manya Krobo area

ID	Na%	SAR	RSC	RSBC	PI	KI	PS	MR	MH	CAI-1	CA1-2	SSP	ESR
MKI	93.0	49.6	10.8	11.1	103.0	38.5	18.3	0.4	30.1	-0.8	-1.3	97.5	38.5
MK2	91.9	42.7	10.3	10.9	101.7	28.7	19.8	1.0	49.9	-0.7	-1.2	96.6	28.7
MK3	50.9	2.2	2.1	3.2	100.4	1.3	0.6	3.5	78.0	-3.1	-0.5	56.6	1.3
MK4	34.6	1.5	1.6	2.1	89.8	1.2	0.3	2.0	66.4	-6.1	-0.7	54.9	1.2
MK5	53.5	2.4	1.3	1.9	105.3	1.8	0.4	2.1	67.9	-4.1	-0.7	64.9	1.8
MK6	63.4	2.3	0.9	1.0	140.9	2.8	0.1	0.3	23.8	-9.0	-0.8	73.5	2.8
MK7	76.8	4.7	1.0	1.1	120.3	5.2	1.1	0.3	24.0	-1.2	-0.9	83.9	5.2
MK8	65.5	4.6	1.7	1.9	106.8	4.4	1.5	0.5	31.8	-1.1	-0.7	81.5	4.4
MK9	85.4	20.4	4.8	5.4	99.7	14.5	8.6	1.5	59.9	-0.8	-1.3	93.5	14.5
MK10	81.2	14.6	8.2	8.9	102.1	8.9	5.7	1.1	52.3	-1.4	-0.8	89.9	8.9
MK11	81.9	20.5	7.4	7.5	101.0	17.1	6.1	0.2	14.6	-1.4	-1.0	94.5	17.1
MK12	73.3	6.3	2.1	2.2	112.6	6.8	1.1	0.3	20.9	-2.2	-1.0	87.2	6.8
MK13	75.6	7.1	2.4	2.8	107.4	5.9	1.9	1.0	48.8	-1.6	-0.9	85.6	5.9
MK14	49.9	2.2	0.7	0.9	102.2	2.3	0.6	0.5	34.4	-1.5	-0.8	69.4	2.3
MK15	67.5	3.1	0.8	1.0	117.1	3.2	0.8	0.6	38.4	-1.3	-0.8	76.5	3.2
MK16	61.6	3.0	1.1	1.4	114.6	3.0	0.5	0.8	43.4	-2.8	-0.8	74.8	3.0
MK17	60.8	3.5	1.6	1.6	114.1	3.9	0.5	0.3	22.1	-3.9	-0.9	79.6	3.9
MK18	69.7	7.4	3.7	4.5	98.2	5.1	3.8	2.7	72.6	-0.7	-0.6	83.6	5.1
MK19	44.8	1.8	0.8	1.4	94.7	1.4	0.7	2.1	67.4	-1.4	-0.6	57.6	1.4
MK20	64.5	3.8	1.9	2.1	116.5	3.8	0.7	0.6	39.2	-2.4	-0.7	79.3	3.8
MK21	80.1	10.5	4.8	5.6	102.6	6.2	1.3	5.3	56.6	-0.8	-0.7	86.2	6.2
MK22	65.7	6.4	4.4	5.9	91.3	3.1	4.2	2.3	70.0	-0.9	-0.6	75.5	3.1
MK23	44.1	1.7	1.3	2.2	96.2	1.1	0.4	3.4	77.3	-3.3	-0.5	52.1	1.1
MK24	71.1	5.1	1.6	2.0	105.1	4.1	1.6	1.4	57.8	-1.4	-0.9	80.3	4.1
MK25	68.8	4.9	2.3	2.5	113.4	4.6	0.6	0.3	23.6	-4.8	-0.9	82.0	4.6

Table 6: Classification of waters based on of EC (Handa, 1969)

EC/μS/cm	Water salinity	Range (No. of sample)	%
00–250	Low (Excellent quality)	125.3-202 (11)	44
251–750	Medium (Good quality)	281-604 (7)	28
751–2250	High (Permissible quality)	982-1709 (6)	24
2251–6000	Very high	2910(1)	4
6001–10000	Extensively high	-	-
10001–20000	Brines weakly conc	-	-
20001–50000	Brines moderately conc.	-	-
50001–100000	Brines highly conc.	-	-
>100000	Brines extremely highly conc.	-	-

Table 7: Sawyer and McCarty's classification for groundwater based on hardness

TH as CaCO3 (mg/L)	Water class	Range (No. of samples)	%
<75	Soft	1.1-7.6 (25 samples)	100
75–150	Moderately hard	-	-
150–300	Hard	-	-
>300	Very hard	-	-

Table 8: Classification of waters based on SAR values (Todd, 1959; Richards, 1954) and sodium hazard classes based on USSL classification

SAR value	Sodium hazard class	Remark on quality	Ranges (No. of samples)	%
<10	S1	Excellent	1.5-7.4 (19 samples)	76
10–18	S2	Good	10.5-14.6 (2 samples)	8
19-26	S3	Doubtful/Fairly poor	20.4-20.4 (2 samples)	8
>26	S4 and S5	Unsuitable	42.7-49.5 (2 samples)	8

Table 9: Salinity hazard classes

Salinity hazard class	EC (μS/cm)	Remark on quality	Range (No. of samples)
C1	100-250	Excellent	125.3-202 (11 samples)
C2	250-750	Good	281-604 (7 samples)
C3	750-2250	Doubtful	982-1709 (6 samples)
C4 and C5	>2250	Unsuitable	2910 (1 sample)

Table 10: Sodium percent water class (Wilcox, 1955)

Na%	Water class	Ranges (No. of samples)
<20	Excellent	-
20-40	Good	34.5 (1 sample)
40-60	Permissible	44.1-53.5 (6 samples)
60-80	Doubtful	60.8-76.8 (12 samples)
>80	Unsuitable	80.1-93.0 (6 samples)

Table 11: Sodium percent water class (Eaton, 1950)

Na%	Water class	Ranges (No. of samples)
>60	Unsafe	57.6 (1 sample)
<60	Safe	71.6-544.5 (24 samples)

Table 12: Soluble-Sodium Percentage (SSP) (Todd, 1960)

SSP	Water class	Ranges (No. of samples)
0-20	Excellent	-
20-40	Good	-
40-60	Permissible	52.0-57.5 (4 samples)
60-80	Doubtful	64.8-89.9 (8 samples)
80-100	Unsuitable	80.2-97.4 (13 samples)

Table 13: Groundwater quality based on RSC (after Richards, 1954)

Class (mg/L)	Remark on quality	Ranges (No. of samples
<1.25	Good	0.7-1.1 (6 samples)
1.25-2.50	Doubtful	1.3-2.4 (11 samples)
>2.50	Unsuitable	3.7-10.8 (8 samples)

Table 14: Permissible limits of residual Mg/Ca ratio in irrigation water

Class	Remark	Ranges (No. of samples
<1.5	Safe	0.1-1.4 (18 samples)
1.5-3.0	Moderate	1.9-2.6 (5 samples)
>3.0	Unsafe	3.4-3.5 (2 samples)