



UNIVERSITY OF GHANA

DEPARTMENT OF EARTH SCIENCE

HYDROCHEMISTRY AND STABLE ISOTOPE ASSESSMENT OF
GROUNDWATER AND SURFACE WATER
BONGO DISTRICT, UPPER EAST REGION, GHANA.

THIS THESIS IS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR MASTER OF PHILOSOPHY DEGREE IN
GEOLOGY

By

AGANA ADAFABILA EMMANUEL

(10273464)

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DECLARATION

This is to certify that, the result of this research is carried out by AGANA A EMMANUEL towards the award of Master of Philosophy degree in Geology in the Department of Earth Science, University of Ghana.

..... Date.....

AGANA ADAFABILA EMMANUEL

(STUDENT)

..... Date.....

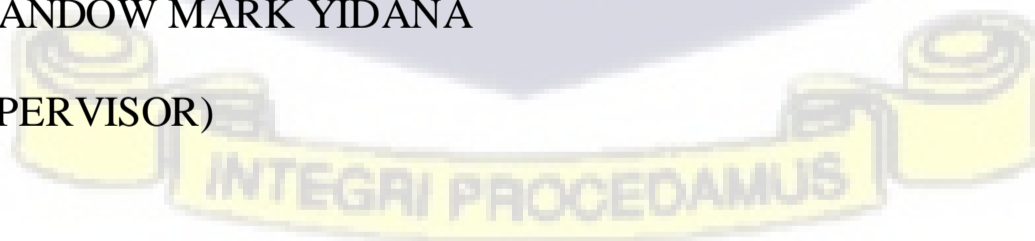
DR. MRS. YVONNE LOH

(PRINCIPAL SUPERVISOR)

..... Date.....

PROF.SANDOW MARK YIDANA

(CO-SUPERVISOR)



ABSTRACT

The hydrogeochemical data of groundwater and surface water of Veia dam water of the Bongo District in the Upper East Region of Ghana were examined to determine the main factors controlling the groundwater chemistry and the resultant water type formed in order to determine the suitability of the water for different uses.

Conventional graphical methods combined with multivariate statistical analysis are the main methods applied to groundwater and surface water hydrochemical and stable isotope (^2H and ^{18}O) data to identify the geochemical characteristics.

Results from 25 groundwater and 20 surface water samples indicated that the concentrations of major ions were low. Based on total hardness and TDS, the groundwater ranged from moderately hard to hard and fell under fresh ($\text{TDS} < 1000 \text{ mg/l}$) water type. By comparing the chemical parameters of groundwater in the study with the WHO guidelines, groundwater was of excellent to good quality for domestic use except in certain locations where fluoride exceeded the permissible limit. Generally groundwater and surface water in the area were suitable for irrigation purposes based on the analysis of sodium absorption ratio, sodium percentage, sodium residue carbonate, permeability index, and magnesium hazard classifications.

Conventional graphical plots of the hydrochemical data suggested that the dominant groundwater type was Ca-Mg-HCO_3 water type which signified modern meteoric water recharge. Hierarchical cluster analysis (HCA) of the hydrochemical data, resulted in two clusters suggesting rock weathering and anthropogenic activities being the main processes controlling the water chemistry. On the basis of ratio the geochemical processes that control the hydrochemistry of groundwater types in the area were dissolution of carbonate, silicate mineral weathering and ion exchanges.

The stable isotopic compositions suggested that there were no apparent hydraulic relationship between surface water and groundwater in the location. However, the result suggested that, both water system were recharged from local precipitation, indicating meteoric origin.



DEDICATION

I dedicate this work to my parents, Mr. and Mrs. Agana, and my brother, Mr. Edward Agana and to all my friends.



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I give thanks to God Almighty for seeing me through this endeavor, praise and adoration are in His name. I am grateful to the Capacity Building Project for the provision of funds for this research work.

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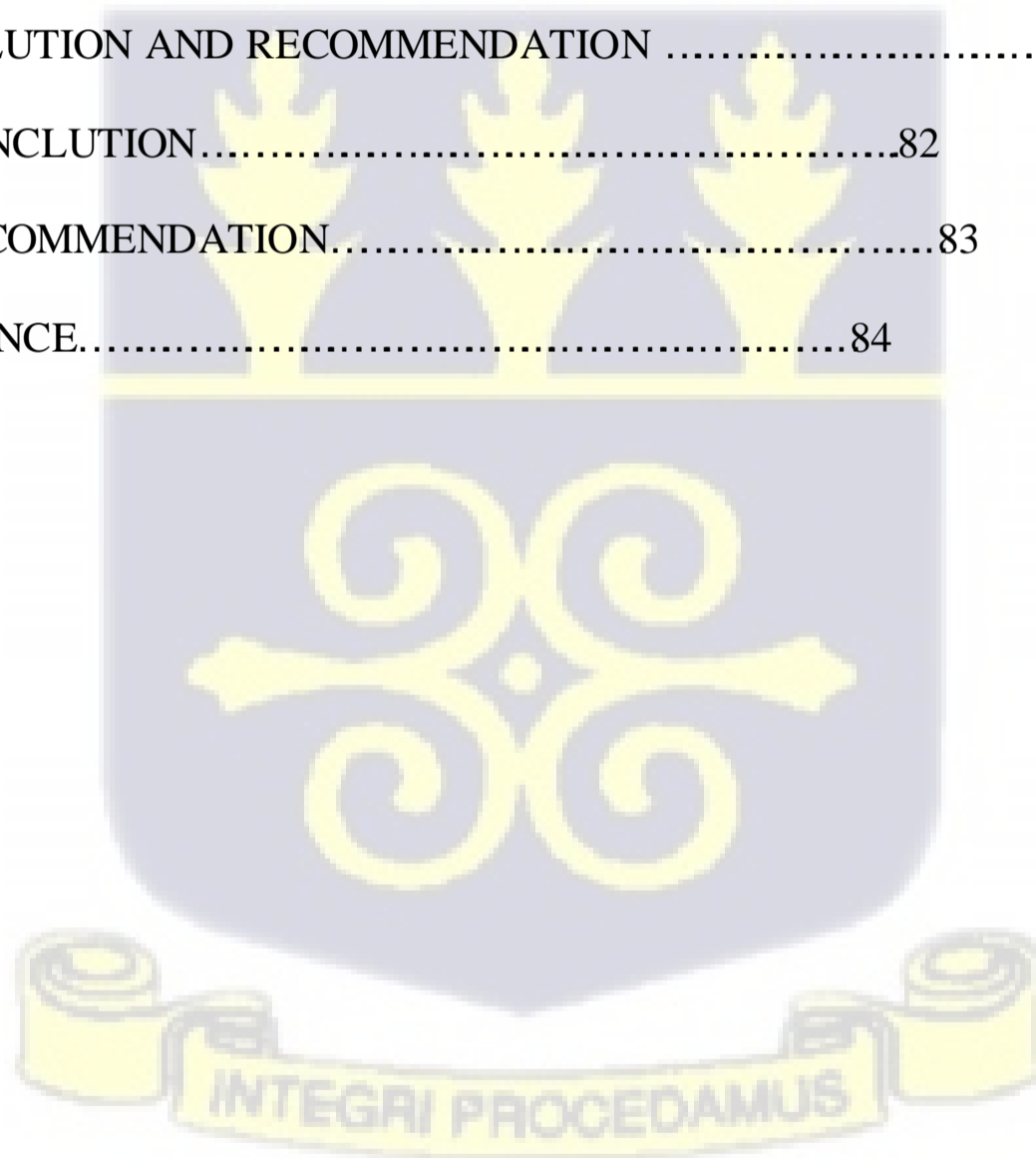
To all my friends and colleagues, especially the "Capacitors" I say thank you for all your advice, encouragement and support. I cannot complete this acknowledgement without mentioning my sister, my best friends and field mates without whom this work would have been a lot more difficult.



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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND AND JUSTIFICATION

Water is a most important natural resource which plays vital roles in enhancing socio-economic growth, food security and promotion of living standard globally. For example, groundwater in Tunisia amounts to 95% of the country's total water resources available, 83% in Belgium, 75% in the Netherlands, Germany and Morocco (Igor and Lorne, 2004). Even though potable water demand for agriculture, hydropower generation and mining are high, it is scarce and unevenly distributed due to climate change and population growth (Singh et al., 2017).

Like many parts of the world, Ghana is experiencing population growth, and its associated increase in demand for water. While most urban communities in the country are supplied with treated surface water, most rural communities depend solely on groundwater resources for their day to day activities. According to the 2010 pollution census, about 84% of the total population live in the rural areas (Ghana Statistical Services, 2010). And this population rely on shallow hand dug well and boreholes for potable water.

Obuobie and Boubacar (2010) indicated that rainfall is a major source of water in Ghana and a dense system of surface water made up of rivers, streams and several perennial springs mostly located in the forested highland areas. However, rainfall varies between the wet and dry seasons and also from one place to another. This causes most surface water bodies that rely on rainfall as their sources of recharge to

dry up before the next raining season. Also these surface water bodies have poor chemical and microbiological quality for domestic use due to high environmental pollution.

Northern Ghana comprises of Upper West, Northern and Upper East Regions, and falls within the semi-arid to arid region of Ghana. These regions are characterized by unfavorable climatic factors such as short rainfall patterns, prolonged dry seasons, high average monthly temperatures, high evapotranspiration which sometimes exceed annual precipitation (Dapaah-Siakwan and Gyau-Boakye, 2000) and a short time surface flow. These have made groundwater a preferred source of potable water for use as compared to surface water resources.

Groundwater resources in the northern area are accessed through borehole fitted with hand pumps that are drilled by World Vision International and other borehole drilling programs (Banoeng-Yakubo, 2000). WHO and UNICEF (2000) estimated that water coverage in the rural areas is about 49%, implying that much more exploitation of groundwater is needed to meet the demand for potable water supply. Poor quality of water for domestic and industrial purposes has led to the occurrence of most reported cases of diseases and also poor crop production (UNESCO, 2006). Previous studies in parts of the Upper East Region revealed the occurrence of waterborne disease epidemics which have been preceded by consumer's showing signs of poor water quality problems (Hrudey and Hrudey, 2007).

The Water Research Institute in Ghana (WRI, 1993) reported that 90% of rural and 25% of urban communities use groundwater resources for their domestic activities

without knowing the quality. According to Lalilha et al., (2004) there has been a rapid increase in non-point sources of groundwater pollution in recent years. Therefore groundwater quality survey has to be carried out to assess such a phenomenon in the rural areas of Ghana, specifically in the Bongo District in Upper East Region

Bempah (2012) noted that, the quality of water may be compromised as a results of improper management of water resources, poor sanitation and the geology. Research has also shown that boreholes drilled in the rural areas are mostly not tested for suitability before using the groundwater as professionals advice (Charrois, 2010). This practice may lead to public health problems.

Several groundwater quality studies within the crystalline basement have been carry out. For example Boat et al., (2014) studied the quality of Vea damp water for domestic purpose using water quality index, Anku et al.,(2009) characterized groundwater quality within the three northern region, Alfredo et al.,(2014) assessed fluoride comtamination in the bongo district. With all these studies, the relationship between Vea dam water and the groundwater within the Vea catchment area which could be an indication of groundwater pollution has not be study. This is because of insufficient hydrochemical and isotopes data to assess groundwater quality, hydrochemical evolution of groundwater and its relationship with surface water in the study area. Hence, part of this work will apply isotopes data to assess the origin and relationship between groundwater and surface water.

Groundwater may have different sources of origins. It can be from ancient marine transgressions, old waters of meteoric origin. The stable isotopes (deuterium and

oxygen-18) can be used to trace the origin of water, the relative ages of different water bodies and the mode of recharge. This therefore plays an essential role in the study of the hydrogeological system. For most groundwater stable isotopes do not change as a result of rock water interaction at normal temperature unless reaction with oxygen and hydrogen bearing minerals either during very long residence times or at elevated temperatures (Fontes, 1980; Gat, 1981; IAEA, 1981). These changes result in isotopic fractionation and can be used to estimate recharge areas and mixing fractions between surface water and groundwater

The lack of adequate knowledge and literature on groundwater quality, chemical evolution and behavior have made groundwater resource management a challenging task. Therefore the study seeks to use hydrochemical data to study water quality and groundwater chemical evolution so as to advise its implication for human consumption and irrigation purposes. It would also establish the relationship between the water resources using stable isotopes.

1.2 STUDY OBJECTIVE

The general objective of the study is to assess the hydrogeochemical characteristics of groundwater in aquifers around the Veia Dam and the surface water in the Dam in the Bongo District of Ghana.

The specific objectives are to:

- assess water suitability for domestic and agricultural purposes
- determine the major water types in the study area
- explore the hydrogeochemical process controlling groundwater chemistry
- investigate ground water-surface water relationship in the area.

1.3 STUDY AREA

1.3.1 Location and Accessibility

The study area is located in Bongo District in the Upper East Region of Ghana. It is bounded by longitudes 0.48°W to 0.54°W and latitude 10.52°N to 10.56° and shares boundaries with Burkina Faso, Kassena-Nankana, Bolgatanga Municipal and Nabdam District to the north, west, south-west and southeast respectively (Fig. 1.1). The District has a total land area of 459.5 km^2 representing about 4% of the total area of upper east region of Ghana.

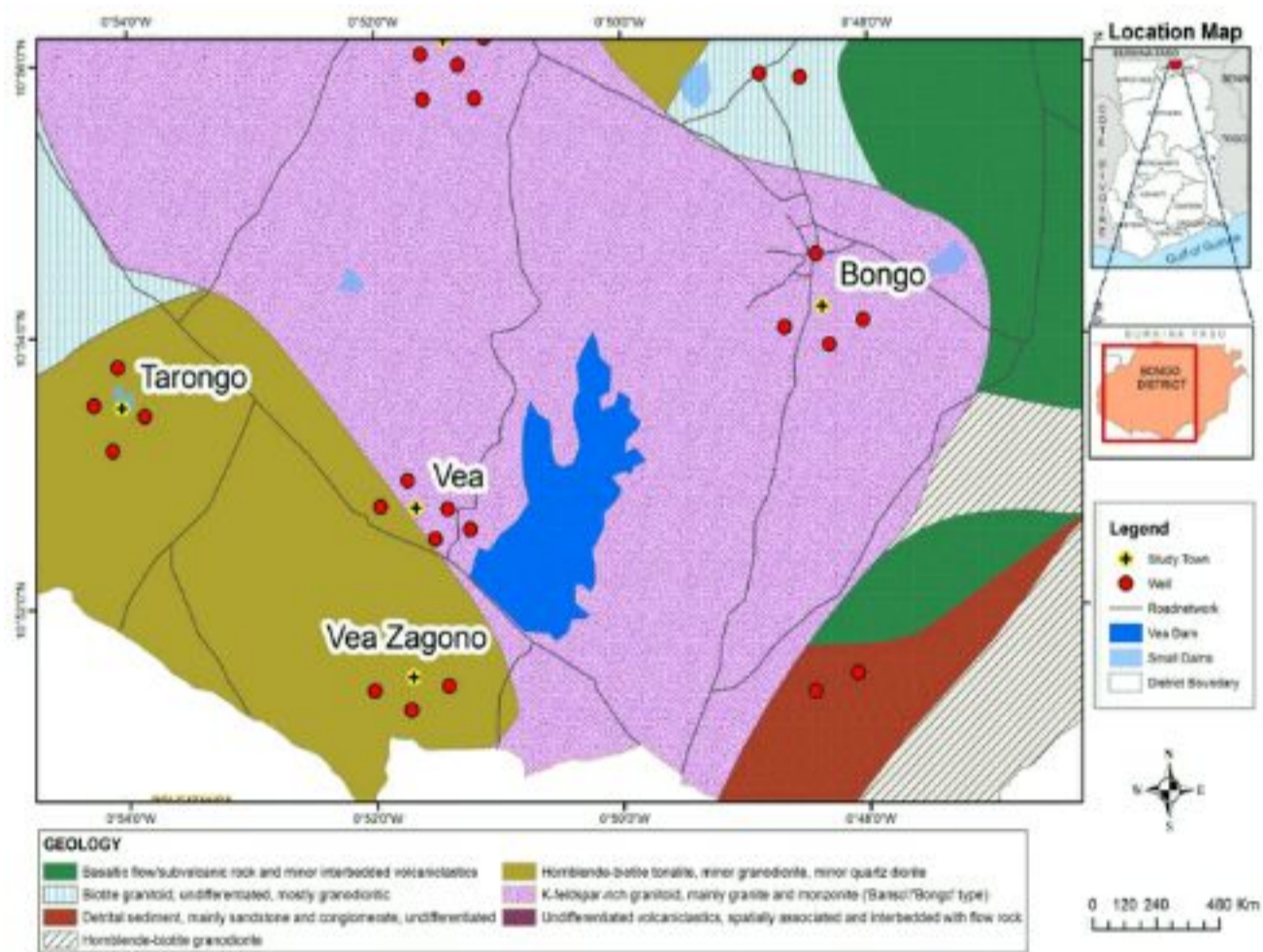


Fig. 1.1: Location Map of the study area showing various lithologies and sampling point.

1.3.2 Climate and vegetation

The study area falls in the semi-arid climatic region also referred to as the Tropical Continental Climatic region. The month of May and October is usually the rainfall season while between November to April is the dry season. During the dry season, dry dusty North-East Trade Winds blow towards the District and the entire region (www.statsghana.gov.gh). The mean annual rainfall in the region ranges from 800 mm to about 1250 mm. The mean monthly temperature, on the other hand, ranges between 27°C and 37°C in August and March respectively with a mean annual temperature of about 29°C. Humidity ranges between 30% in the dry season and 80% in the wet seasons. Evapotranspiration is higher than rainfall throughout the year except in the months of July, August and September in most parts of the region (ghanadistrict.com).

The vegetation of the study Districts is classified as Guinea Savannah Woodland characterized by drought resistant trees such as Baobab, Shea, Dawadawa and Acacias which are at distance from each other (Pelig-Ba., 2009). They are also widely spaced short deciduous trees of different species and of varying heights.

1.3.3 Topography and drainage

The topography of the study area is fairly flat with some few high land areas with an average topographic height ranging between 180 m and 300 m above mean sea level. Small rounded granitic rocks are found on the high plains with perennial river and their ephemeral tributaries drain the entire region.

1.3.4 Soil

The parent materials of the soils are the Bongo granites characterized by high potash and phosphate content making the soil very productive (Brammer et al.,1962). Generally, the soil layers consist of about 3 inches of coarse sandy loamy top soil with little stained made by human activities overlying reddish brown, very coarse sandy clay containing incompletely weathered feldspar particles. Texturally the soils are silt or sandy loam when developed over voltaian rock and coarse-grained sandy-loam when developed on granite (Kesse et al., 1985).

1.3.5 Geology

The study area is extensively underlain by basement crystalline formation which covers about 54% of the country land area. It is made up of the granite-migmatite complex rocks and rocks of the Birimian Supergroup (Junner, 1940; Kesse, 1985) (Fig. 1.1). Rocks of the Birimian Supergroup are made up of two major lithostratigraphic units: Birimian Sedimentary rocks and Birimian Volcanic intrusion (Kesse, 1985). These rocks have been extensively studied by various workers (Junner et al., 1935; Leube et al., 1990; Hirdes et al., 1992;) because they host most of Ghana's mineral deposits. From these studies, the Birimian supracrustal rocks are said to be metamorphosed under greenschist-facies conditions and intruded by granitoids as a result of the Eburnean tectonothermal event.

The Birimian sedimentary rocks in the area are steeply dipping with alternating sandstones and sheared conglomerates, slates and argillaceous beds and some phyllites, schistose greywackes,. The rocks are primarily of pelitic origin, having been mud and silts with beds of coarser sediment (Kesse, 1985). The Birimian

Volcanic Belts rock is dominantly of meta-basalts and meta-andesites with volcanic and pyroclastic origin.

According to Griffiths et al. (2000), large masses of granites and basic intrusive rocks intruded the Birimian formation. The K-feldspar rich Bongo type granitoid is the most abundant granites which covers a large part of the area in which most of the bore holes were drill (Banoeng-Yakubo, 2000). The granitoid in the area occur as large, highly foliated migmatized and generally potash-rich biotite and muscovite granites granodiorites. These granites, usually with fresh feldspars, are characterized by enclaves of schist and gneisses (Junner, 1940; Kesse, 1985). The undifferentiated volcanoclastic granites are also characterised by pink porphyroblastic alkali feldspars in finer grained matrix, they are foliated and comprises of boulders with varying sizes.

The hornblende-biotite rich granitoids intruded the Birimian meta-volcanic rocks in the area. These rocks consist of soda-rich, hornblende-biotite granite or granodiorites, which grade into quartz diorite and hornblende diorite. Also found in association with these rocks are porphyritic biotite and biotite gneisses (Leube et al., 1990)

1.3.6 Hydrogeology

The occurrence of groundwater in all except the Coastal Sedimentary areas aquifers depends on Secondary structures made up of fractures, veins and faults. The development of secondary permeability in these rocks is enhance by the nature, aperture, length, and the degree of interconnection of the fractures (Atobrah, 1980) and content of the fractures as well as the extent of weathering. The development of

fractures and faults is a direct consequence of activities during regional tectonic processes.

In these rocks, the nature and thickness of the zone, rock fracture, joints, quartz veins determines the mode of occurrence of groundwater. The water-bearing and yielding capacities of these rocks depend on the extent of these secondary permeabilities (Banoeng-Yakubo et al., 2000; Banoeng-Yakubo et al., 2001).

In the crystalline basement provinces groundwater occur mainly in the saprolite, saprock and in the fractured zone bedrock. The upper saprolite act as a semi-confining layer due to its low permeability, while the lower, usually saturated part of the saprolite is characterized by lower secondary clay content, thus creating a zone of enhanced hydraulic conductivity. Generally, areas underlain by the Birimian rocks display deeper seated weathering than areas underlain by the granitoids.

According to Banoeng-Yakubo. (1989) and Norgbe, (1998), there are three types of aquifers identified in the basement area. These are: the weathered zone, fractured zone, and bedrock – weathered zone interface (zones intruded by quartz – veins and pegmatites) aquifers. The regolith which comprises of topsoil and highly weathered mantle or saprolite make up the weathered zone aquifer. Depending on the mica and clay contents this aquifer is characteristically semi-confined with high static water levels (1.5 m –4.0 m) below ground level.

The yield of this aquifer is related to the thickness of the weathered rock and nature of the topography. This subsequently implies that aquifer development within the area

depends on weathering of the rocks. The fractured zone aquifer is the deepest of the three aquifers. These aquifers are located within the sap-rock characterises as semi-confined to confined. Borehole characteristics show that the depths to this aquifer vary from 12 m –30 m and have relatively high yields. The quartz-veined aquifers or bedrock- weathered zone aquifer is the third major aquifer in the study region. This aquifer type can occur as semi-confined or confined and is the most productive in the region, with relatively high yields (Norgbe, 1996).

Most groundwater projects terminate drilling when sufficient water is obtained for rural water delivery. According to Agyekum., (2004) the depths of boreholes range between 35 m and 62 m with an average of 42 m in the Birimian rocks. However, in the granitoids the range is between 35 m and 55 m, with an average of 50 m (Carrier et al., 2008). In some areas underlain by the regolith borehole depths are relatively shallow.

The productive zones of the Birimian has a transmissivity range between 0.2 m²/d and 119 m²/d, with an average of 7.4 m²/d. In these aquifers, storativity ranges between 0.003 and 0.008. Transmissivity within the regolith is slightly higher than that observed in the integrated aquifer system, and ranges between 4 m²/d and 40 m²/d with an average of about 10 m²/d. For the aquifer systems in the Birimian, borehole yields are generally low and range from 0.48 m³/h to 36.4 m³/h with a mean yield of 7.6 m³/h. Differences in the degree of weathering within the granitoids probably account for the lower yields observed in these rocks, (Yidana et al., 2008)

The aquifers within the upper fractured bedrock generally contain subhorizontal fractures. The transmissivity reduces with depth due to the the increasing overlying weight. However, subvertical fracture or fault zones can be present at great depths which provide significant amounts of groundwater. Generally boreholes have an average depth of less than 80 m (Agyekum et al., 2004).

In the Birimian formation, rocks intruded by quartz-veins or pegmatites are also known to yield relatively higher quantities of groundwater. In some cases, hydraulic connectivity between the lower saprolite and the saprock may vary with weathering intensity and fracture characteristics and lead to separate aquifer systems. When taken separately, the regolith aquifer can exhibit a higher transmissivity than the fractured rock aquifer because of its generally greater saturated thickness. The impervious nature of the upper part of the regolith or the presence of an indurated layer at the base of the residual soil zone can lead to the development of a shallow perched aquifer if the upper part of the residual soil zone consists of coarsely textured material.

CHAPTER TWO

LITERATURE REVIEW

2.1 HYDROGEOCHEMISTRY

Groundwater is by far the most extracted raw material and it is estimated that about 7×10^{12} m³ of groundwater is drawn from the world's aquifers each year (Jean-Claude, 1995). The quality of groundwater is determined by the processes and reactions that the water undergoes from the moment it condenses in the atmosphere to the final consumer. Generally, the movement of groundwater below the sub-surface along its path increases the concentration of chemical species as it interacts with the host rocks and other materials. Hence, groundwater chemistry could reveal important information on the geology of the aquifers, the recharge, and suitability of groundwater for domestic, industrial and agricultural purposes (Aghazaded and Mogaddam, 2010).

The study of hydrogeochemical evolution of groundwater system is usually based on information concerning groundwater chemistry (Hossien, 2004). This depends on a number of factors that are both natural and anthropogenic. These factors include but not limited to; geology of the aquifer, sources of recharge, mining, agriculture, industrial waste disposal etc. Such factors and their interactions result in a complex groundwater chemistry affecting the natural quality of water (Sunneetal., 2005). It therefore, means that even though groundwater is a common resource, the chemical properties of the water which determine its suitability for use can change. Hence, the World Health Organization (WHO, 2014) guideline of water potability has been used by several workers (e.g. Anku et al., 2009; Yidana et al., 2009) in determining the quality of water for use.

In Northern Ghana, the high demand for groundwater for domestic purpose calls for an examination of the suitability of these resources. Yidana et al. (2007) noted that understanding of the hydrochemical properties of the rock that form the aquifers through the studies of water chemistry is a good requirement for efficient development and management of groundwater for exploitation.

Ghanem and Merkel (2000) and Raji and Alagbe (1997) reported that the composition of the medium through which the water move to the aquifer and the rock composition has an influence on the chemical composition of the water and hence its quality. Therefore dissolve minerals and chemicals composition gives an imprint of the host rock.

Suyfzand (1999) noted that factors such as increase length of flow path of water and increase in depth of the aquifer has a strong impact on the ionic composition of groundwater, therefore the chemistry of groundwater is different at different point space and time both in ionic concentration level and salt content.

Groundwater quality assessment is based on its physical, chemical and biological characteristics. Usually studies on groundwater quality for a particular purpose are carried out by comparing selected parameters such as pH, electrical conductivity, salinity, alkalinity, temperature and major ions (Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} , HCO_3^- and F^-) with a standard values such as WHO recommended values.

Anku et al., (2009) carried out water quality analysis of groundwater within the crystalline basement rocks in the Northern Region of Ghana. The results indicated

that the physical and chemical parameter were within WHO acceptable limits with the exception of fluoride and nitrate in some locations. Another method such as water quality index was also used to assess the suitability of Veia dam water for drinking purposes by Boat et al., 2014. Results indicated that WQI was found to be 54.21 meaning that raw water from the dam was of poor quality for drinking. The limitation of water quality index is that; the method is insensitive to individual parameters and does not take into account local natural background water quality effect (Kerr and Biggs, 199).

The quality of crops production, maintenance of soil productivity and protection of the environment depend on the quality of irrigation water used. Therefore, criteria such as Salinity hazard, Sodium hazard/Sodicity, pH, Alkalinity, Specific conductance have been used to describe effects of irrigation water on crop production and soil quality (Bauder, 2011). Sodium enrichment in soils brings about permeability problems; Na^+ ions in the water tend to replace Ca^{2+} and Mg^{2+} ions in the soil leading to clay expansions and eventually minimizing air and water circulation.

Hess (1989) noted that specific conductance and SAR combination can be used as a tool to classify water suitability for irrigation and that EC near 2000 $\mu\text{S}/\text{cm}$ and SAR more than 10 represent high sodicity and will not be good for irrigation.

Work on the hydrochemical evolution of the aquifer system in northeastern Algeria was carried out by Fehdi et al., (2009) using major ion chemistry and isotopic data. The study stated that the increase in salinity was seen to be related to the salt rock dissolution and cations exchange process between groundwater and clay minerals.

Krothe and Bergeron (1981) also classified groundwater into types based on the dominant chemical ions such that water with similar chemical composition formed cluster given a similar hydrochemical facies. The hydrochemical facies reflect the effect of chemical processes in the host rock and the flow pattern of the groundwater. Hence water within the crystalline rocks have been classify as Ca-Mg-HCO₃ facies according (Anku et al., 2009)

Rouabhia et al. (2009) combined chemical and environmental isotope data to determine the origin of dissolved species in groundwater. It was revealed that, the chemical evolution of groundwater was primarily controlled by water rock interactions. Interpretation of ¹⁸O and ²H also suggested that the recharge of the investigated groundwater may result from different mechanisms.

Kortatsi (2004) used these techniques to establish that a mildly acidic and low conductivity ground silicate mineral weathering were probably the main process through which major ions enters the groundwater and that groundwater in the area was recharged from a meteoric origin.

Hydrogeochemical evaluation of groundwater is copiously studied globally (Back and Hanshaw, 1965; Collins, 1975; Johnson, 1975; Moore, 1985; Sastri and Lawrence, 1988; Stuyfzand, 1989; and Lavitt and others, 1997). Similar works were also carried out by (Yidana et al., 2009; Loh et al., 2012; Apambire et al., 1997; Acheampong and Hess (1998); Zango et al., 2014; Apellig-ba et al., 2010; Yakubu et al., 2009) on the crystalline basement aquifers in Ghana.

Acheampong and Hess (1998) noticed that the factor controlling groundwater chemistry within the southern Voltaian Basin and the Afram Plains are weathering of albitic feldspars. However, Yidana et al. (2008) identified silicate mineral weathering as the primary control on the hydrochemistry of groundwater from the Afram Plains using mass balance and multivariate techniques. Mineral weathering and rainfall were revealed to be the main factor controlling water chemistry within the crystalline basin in Gushesgu district Salifu et al. (2014).

Tweed et al. (2004) used major ion chemistry to qualitatively interpret groundwater residence time within an aquifer with distinct mineralogy. In combination with isotopes the flow paths and inter-aquifer system interaction was define in the Dandenong Ranges, Southeast Australia.

Firusramli et al. (2014) employed hydrochemistry and statistical analysis of major ion to characterize aquifer in the Amol-babol plain, Iran. The study suggested that calcium and magnesium were the dominant cation and bicarbonate the dominant anion in the area which could be related to the presences of carbonate minerals, weathering of silicates and ion exchange as the hydrochemical processes influencing the groundwater chemistry in the area.

Major ion ratio are useful in establishing chemical similarities and causes of the occurences of these ions in water. Researchers such as Edet and Okereke (2005), Petrides et al. (2006) and Yidana (2012) used major ion ratio to identify the sources and geochemical process operating in the groundwater system.

Ewusi et al. (2013), studied the groundwater quality for drinking and irrigation purposes in Obuasi municipality of Ghana within the crystalline rocks. Parameters like sodium adsorption ratio, percent sodium, electrical conductivity, total hardness, total dissolve solutes and stoichiometric relations were calculated. The result of the study classified water as suitable for domestic and irrigation use and concluded that, silicate mineral weathering and ion exchange are the main factors controlling groundwater chemistry.

Apambire et al. (1997) studied the fluoride contamination in the Bongo District and its relationships with the underlying geology and precipitation patterns. The findings in the study indicated that granite formations contain from 2 to more than 20 times the amount of fluorine in the surrounding rock formation, therefore fluoride contamination in the Bongo District was attributed to the geology of Bongo granite.

Aside the estimation of sodium content to determine the favourability of water for irrigation, the excess sum of carbonate and bicarbonate over the sum of calcium and magnesium referred to as Residual Sodium Carbonate (RSC) can also be used to predict the suitability of groundwater for crop irrigation (Ragunath, 1987). In addition to the above methods of identifying suitable irrigable water, the Permeability Index (PI) can also be used. PI is a measure of the total Na^+ and bicarbonate concentration relative to the total cations present in the water (Subramani et al., 2005).

Ajayi (1998) characterized groundwater in coastal Nigeria and concluded that they were generally of poor quality with respect to ionic constituents. The study further

suggested that groundwater from some selected boreholes in Agbalu are not suitable for domestic use without treatment because the water was brackish. Singh and Singh (2008) characterized the quality of water in Gwalior region in India using sodium adsorption ratio (SAR) and residual sodium carbonate (RSC) and concluded that the groundwater is considered to be suitable for irrigation purpose. However, its suitability for drinking purposes without treatment is minimized because a few parameters fall higher above the limit of WHO (2004).

Also, Johnson and Zhang (2010) classified water suitable for irrigation in Oklahoma using a plot of percent sodium versus electrical conductivity (EC). Water with percent sodium range above 85% and EC above 3000 $\mu\text{S}/\text{cm}$ was classified poor, the water samples with EC above 5000 were considered very poor and the samples with sodium percent below 85% and EC below 3000 $\mu\text{S}/\text{cm}$ were poor to excellent. They concluded that water of undesirable quality may be used successfully if the chemicals can be neutralized by conditions such as gypsum content of the water and/or soil, soil characteristics and effective rainfall.

Similar works carried out in other parts of the world include; Elango et al. (2003) identified the major subsurface hydrochemical processes responsible for the concentration of major ions in groundwater in Palar River Basin and Chithar River basin, South India. Cireli and Miretzky (2004) have inferred that cation exchange reaction between calcium and sodium in the hydrochemical evolution of groundwater through Pampean loess sediments is responsible for high sodium content compared to chloride content.

The important hydrogeochemical processes that control groundwater composition in the Mar del Plata aquifer, Argentina, is suggested by Martinez and Bocanegra (2002) to be cation exchange processes and calcite dissolution.

Stable isotopes of Oxygen and hydrogen are used as tracers to study hydrogeological processes such as precipitation, groundwater recharge, groundwater-surface water interactions, climatic change and basin hydrology because they are not altered by rock-water interaction and considered as conservative element.

Yeh et al. (2009) used stable isotopes of oxygen and hydrogen as tracers to determine the seasonal contributions of precipitation and river water to the groundwater in Chih-pen and Jin-lun creek basin in Taiwan. The correlation of stable isotopes were analysed to assess the sources of groundwater recharge and hydrological variation, also using mass balance analysis for the oxygen and hydrogen isotopic composition the groundwater recharge percentages of every recharge sources were evaluated.

Butler et al. (2000) used stable isotopes ($^2\text{H}/\text{H}$ and $^{18}\text{O}/^{16}\text{O}$) to trace the sources of pollution in Bellville (Cape Town). The study further employed radioactive isotopes to trace the leakage in urban water system and the effect of physiography on small-scaled groundwater system.

Sklash et al. (1976) used isotopes to determine the relative amount of groundwater contribution to stream flow at various point and at different seasons. McCarthy et al., (1992) also used dD and d^{18}O values to show that the Columbia River water

contributed 50% of the water pumped from municipal wells from 1 km away, near port, Oregon.

Petrides et al. (2006) used stable isotopes and ions ratios to study the origin of groundwater in the Murray Basin. They indicated that the water was of meteoric origin and that the causes of high salt content in the basin was due to evapotranspiration of rain water and dissolution of halite.

Kaka et al. (2011) assessed interaction of groundwater and Volta lake water using stable isotopes in the southwestern margin within Manya-Krobo area. The study suggested that groundwater was recharged predominantly from rainfall but had undergone some degree of evaporation in the atmosphere or in the soil zone before reaching the groundwater. Also deduction were made that infiltration of lake water to groundwater was possible because boreholes that received recharge from the lake had isotopic composition almost close to that of the lake water.

Edjah et al. (2015) studied hydrogeochemistry and isotope hydrology of surface water and groundwater systems in the Ellembelle Distric. Result of the stable isotope composition indicated that, all the rivers appeared to be evaporated, 60 % of the hand-dug wells and 70 % of the boreholes plot along and in between the global meteoric water line and the local meteoric water line, suggesting mixing and rapid recharge from meteoric origin.

Yidana et al. (2008) investigated on stable isotope characteristics of groundwater in the Voltaian Basin. They concluded that groundwater in the shallow aquifer system

originated from recent precipitation which had endured evaporative enrichment of the heavier isotopes. It was also suggested that groundwater did not contribute to local stream flow in the basin and that if there is any relationship between the surface flows and subsurface water; it is certainly the fact that both receive recharge from current precipitation.

Statistical analysis is a very useful tool for assessment of groundwater chemistry and mostly used in the literature. Statistical technique can reveal an important information on spatial distribution and the association between different parameters (Balasu et al., 1989).

Multivariate statistical analysis techniques uses multiple variables to study the variations, relations, and distributions of hydrogeochemical data (Hamdan, 2012). Such techniques include Hierarchical Cluster Analysis (CA), Factor Analysis (FA) and pearson correlation matrix. They are effective techniques for manipulating, interpreting and representing large data (Belkhiri et al., 2010). Principal component analysis (PCA) have been used to distinguish various processes (natural and anthropogenic) that affect the physico-chemical properties of the groundwater (Morel et al 1996; Yakubo et a; l., 2009Yidana et al., 2012)

Yidana et al. (2009) used the technique to characterize the hydrochemistry of groundwater in northern Voltaian basin. The study revealed that groundwater hydrochemistry was controlled by silicate and carbonate minerals as well as cation exchange. They also concluded that the hydrochemistry of the groundwater is controlled by the geology through the process of ion exchange.

Statistical method was also used by Pellig-Ba et al., 1998, to study groundwater from parts of the crystalline rocks in the Upper East Region, which show that groundwater have high trace element concentrations. Fianko et al. (2010) used similar method to show that groundwater in Tema district of Ghana is fresh and generally suitable for domestic use.

Yidana et al. (2012) similarly identified the hydrochemistry and causes of fluoride enrichment in groundwater from the middle Voltaian Sedimentary aquifers in the Northern Region, Ghana using factor model. Results of the Q-mode hierarchical cluster analysis identify three locations of the groundwater flow.

Cloutier et al. (2008) applied HCA and principal components analysis (PCA) to classify the groundwater samples, and to identify geochemical processes controlling groundwater chemistry. It was revealed that the evolution of groundwater was controlled by the geology.

Yidana et al., (2006) applied hierarchical cluster analysis (HCA) and principal component analysis (PCA) to assess the main processes that control the chemistry of surface water resources from the Ankobra basin and concluded that the hydrochemistry of the basin was controlled by the weathering of minerals and the decay of organic matter. Banoeng-Yakubo et al. (2009) applied multivariate and mass balance approaches to study the main determinants of the hydrochemistry of groundwater in some sections of the Volta Region of Ghana.

Chen et al., (2006) used multivariate statistical analysis to study the relationship among trace elements and factors controlling trace element distribution in groundwater and concluded that multivariate statistical techniques are efficient ways to display complex relationship among many groundwater parameters. They also noted that the attention of Q-mode factor analysis is used to interpret the inter-object relationships in a data set while R-mode factor analysis was used to interpret inter-variable relationships.

Also graphical displays can be used to interpret groundwater flow path and the process that affect the hydrochemistry of groundwater (Piper 1944; Gibbs 1970). Mahlkecht et al. (2004) noted the usefulness of graph in the interperation of groundwater evaluation and the relationship between groundwater and rock. Even though the graphical technique remains a preferable technique for analyzing groundwater chemistry by many, one disadvantage of the techque is the limited number of parameters that can be shown at a time (Guler et al., 2002).

CHAPTER THREE

METHODOLOGY

Research methods and procedures adopted in sampling and analyses of groundwater either in the field or laboratory is a major concern in groundwater investigation. The reason is that the primary sources of error in groundwater quality studies is seen to be emanating from the procedures used in collecting and analysing representative samples. Procedure for collecting reliable data in this study during field and laboratory work were followed as outlined by Chapman (1992). These procedure and analytical method employed are discussed in this chapter.

3.1 DESKSTUDY

The baseline data for this research was built by reviewing books, reports and journals containing literature related to the research. To determine the general geological formation and hydrochemical facies prevailing in the study area, geological maps were obtained from the Geological Survey Department. Sampling kits and other material to be used in the field were obtained.

Furthermore, reconnaissance field work was carried out prior to actual sampling, this helped to calibrate the sample kits to be used and keep them in a workable state, and also to identify the types of surface water (Vea dam) and groundwater (boreholes) to be sampled and also access their locations.

3.2 FIELD WORK

To assess water chemistry, representative water samples were collected from groundwater and surface water bodies in the area. Sampling points were selected to cover the various geological formations in the study area in order to make a

meaningful and more realistic analysis with reference to characterisation of groundwater quality.

Water sampling was purposely undertaken during the dry season since there is a high abstraction from the domestic wells and the water may possibly be representative from the aquifer and also there are more stable water quality conditions as compared with the rapid changes in water chemistry during the raining period. Therefore, October 2015 was selected to conduct an initial sampling programme. Water sampling commenced on the 19th of October and lasted ended on the 21st of October.

A total of 150 samples were collected from 26 domestic boreholes and 15 sampling points from Veia dam. For groundwater, samples were collected directly from the pump outlet using acid-washed polyethylene plastic bottles of 120 ml. At each sampling point three different samples were taken for cation, anions, and isotopes (¹⁸O and D) analysis. These included unfiltered samples for isotopes, samples acidified with dilute nitric acid for cations and unacidified samples for anion analysis. At each sampling site, borehole was purged to remove stagnant water by at least twenty minutes of pumping prior to sampling. The stability in the value of pH, temperature and electrical conductivity (EC) was an indication that, the water being delivered was coming from the aquifer.

Surface water samples were also collected from five different points within the dam; at the inlet by hauling a plastic bucket attached to a rope over the bridge and collected in the deepest water, the centre using a plastic scoop attached to a short pole by boat, the outlet of the dam and the remaining two locations were selected randomly. Along

the tributary samples were not taken because at the time of sampling the rivers were dry. Figure 1.1 shows the groundwater sampling point.

Sample bottles were tightly capped, labeled and preserved in a thermo-insulated container with ice packs immediately after sampling. However, samples for stable isotopes were also stored in a thermo-insulated container without ice packs to prevent condensation of the lighter isotopes. This was done to avoid contamination and also to keep the chemical character of the sample from changing. Samples collected were then transported to the laboratories of the Ghana Atomic Energy Commission (GAEC), Kwabenya in Accra.

At each sample point, the Global Positioning System (Germinetrex 20, U.S.A.) reading for the sampling points were taken and recorded together with the date and elevation. Parameters such as temperature, electrical conductivity (EC), total dissolved solids (TDS), were measured in the field. This is because physical parameter may change with time. conductivity were measured with a universal conductivity meter. Ph was also measured with pH meter. Both sampling kits were calibrated with standard solution and sterilizes with distillation water.

3.2.1 Limitation

The limitation during field works was lack of rain water data for stable isotope analysis. Rain water data stable isotope analysis helps to establish a local meteoric water line for the study area. Static water level was not able to be measured because

the boreholes were fitted with hand pumps and it was not possible to dismantled and sample. Also, some part of the study area were not sample because they had water supply by the Ghana Water Company and had limited or no boreholes.

3.3 LABORATORY WORK

Prior to laboratory analysis, standard solution, and reagents for the experiments were already prepared by the laboratory technicians. The procedure used to analyses for various parameter in the samples include; titration method for Alkalinity, bicarbonate, chloride, total hardness, calcium and magnesium, flame photometer for analysing potassium and sodium and UV-Visible spectrophotometer method was used for sulfate and nitrate.

Alkalinity and bicarbonate contents of the water samples were determined by titration. 5 ml of the water sample with two drops (~ 1 ml) of methyl orange indicator was titrated against 0.02M HCl solution, till a deep yellow color changed to pale yellow and to orange respectively. The volume of HCl used to obtaine the pale yellow colour was used to calculate alkalinity concentration using the equation below;

$$\text{Alkalinity (CaCO}_3\text{)} = \frac{A * M}{V} * 50 \quad (3.1)$$

Where: **A** is the average titre value in mL, **M** is the molarity of acid (HCl solution); and **V** is the volume in mL of the water sample.

The valume of HCL used to obtained orange color was to calculate the bicarbonate concentration using the equation:

$$(\text{HCO}_3^-) = \frac{V_{\text{HCL}} * M}{V} \quad (3.2)$$

Where V_{HCL} is the volume of HCl used, M is concentration of HCl and V is the volume of samples used.

Chloride ion concentration was determined by argentometric titration method.

Fifty milliliters (50 ml) of the sample with one milliliter (1 ml) of K_2CrO_4 indicator solution was titrated with standard AgNO_3 to a pinkish yellow end point. Reagent blank value was established by titrating 50ml of distilled water with 1ml of K_2CrO_4 indicator against standard AgNO_3 . The amount of chloride in the unknown water samples was determined using the equation below.

$$\text{Cl (mg/l)} = \frac{(A-B) * M * 35.450}{V} \quad (3.3)$$

Where: A is the average titrant, B is the titre value of the blank solution, N is the molarity of AgNO_3 (0.0141M), and 35.45 is relative atomic mass of chlorine.

To determine Calcium (Ca^{2+}) content in water samples, two milliliters of NaOH and 0.1g of mirexide indicator was added to 50 ml of the sample. The mixture was titrated with EDTA until the color changed from Salmon to orchid purple. The end point was checked by adding 2 drops of titrant in excess to make sure that no further color

change occurred. The amount of calcium in each water sample was calculated using the equation below.

$$Ca (mg/l) = \frac{A * 105 * 400.8}{V} \quad (3.4)$$

Where A = ml of EDTA titrant used

V = volume of samples

Total hardness was analysed using the titrimetric method with Eriochrome black T as the indicator. Fifty milliliters of the sample was mixed with 1g of Eriochrome Black T indicator and 1ml of a buffer solution to produce a pH of 10. The mixture was then titrated with a standard 0.01M EDTA until the last trace of purple disappeared and the color turned bright blue.

$$Total\ Hardness = \frac{EDTA * B * 1000}{V} \quad (3.5)$$

Where V = volume of sample, B = mg of CaCO₃ equivalent to 1ml of EDTA titrant.

The difference between total hardness and calcium hardness gives Magnesium hardness which is expressed in mg/l. Magnesium concentration was then obtained by multiplying magnesium hardness by 0.243.

$$Mg (mg/l) = \text{magnesium hardness} \times 0.243 \quad (3.6)$$

Sodium (Na) and potassium (K) concentration in the water samples were also determined by flame emission absorption photometric method, using the Sherwood 420 Flame Photometer (Sherwood, UK). The machine was calibrated with a known concentration of Na and K solution, after which water sample was analysed. About 5 mL of the water sample was transferred into a test tube followed by the addition of 2 mL of the suppressor solution. The mixture was homogenized for a minute and then aspirated into the flame of the photometer. The contents of Na and K were read and recorded.

About 10 ml of the standard SO_4^{2-} solutions and water sample were measured respectively and mixed with 1 ml of acid salt solution, 0.5 ml of glycerol solution (conc.) and 0.5 g BaCl_2 in two separate test tubes. An appropriate aliquot of the cloudy solution was transferred into 1 cm cell and the absorbance of the coloured solution was measured at a wavelength of 420 nm on the UV-visible spectrophotometer. The absorbance of each calibrated solution was plotted against the concentration. The concentration of the sulfate in the water samples was deduced from the graph.

Nitrate was determined using the AOAC Official method. About 5 mL of the samples was mixed with 1 mL of 30% NaCl and 5 mL of 6.5 M of H_2SO_4 . The test tubes were swirled to ensure thorough mixing of the reagents. 0.5 ml of the brucine-sulfanilic acid reagent was added to the content of each tube (except blank). The mixture was heated in a water bath at 95 °C for 25 minutes. An appropriate aliquot of the yellow colored solutions was transferred into a 1 cm cell and measured in a spectrophotometer at a wavelength of 410 nm.

The stable isotope (^2H and ^{18}O) compositions of the samples (both surface water and groundwater) were measured using the Liquid–Water Stable Isotope analyzer (LGR DT-100 liquid water stable isotope analysis, Los Gatos Research Inc., USA) based on the off-axis integrated cavity output spectroscopy (OA-ICOS) via laser absorption (IAEA, 2009).

The LGR instrument measures the molecular concentrations of ^2H and ^{18}O using a wavelength of about 1390 nm. Molecular concentrations are then converted into atomic ratios of ^2H and ^{18}O and a post-processing procedure is to calculate delta-scale (δ) values with respect to Vienna Standard Mean Ocean Water [VSMOW] (Coplen, 1996) using the equation below.

$$\delta = \frac{R_{\text{sample}} - R_{\text{VSMOW}}}{R_{\text{VSMOW}}} \quad (3.7)$$

Where: R is ^2H and ^{18}O

3.3.1 Quality Control (Qc) And Quality Assurance (Qa)

The following QA/QC guidelines were undertaken during sampling to produce acceptable results.

- ü All glassware and sampling containers were soaked in nitric acid (10 % HNO_3) and rinsed with deionized water before use. This was to ensure contaminant free sample bottles which could affect the concentrations of various ions in the water samples.

- ü During sampling, boreholes were purged for ten minutes to flush the stagnant water retained in pipes in order to have a representative water from aquifer.
- ü Standard chemical solutions prepared and validated with Standard Reference Materials (SRM) and Certified Reference Materials (CRM) were used to calibrate instrument for the process.

3.4 DATA PROCESSING AND ANALYSIS

Mathematical and statistical procedures are the two methods used in processing and analysing the data obtained. Graphs and maps were also made to show relationships between variables.

3.4.1 Mathematical Method

The anion-cation balance method was used to check the accuracy of the results obtained from the laboratory analysis. The concentration obtained in mg/l from the laboratory was first converted into milliequivalent per liter using the formula:

$$\frac{\text{Meq}}{\text{l}} = \frac{\text{mg/l} \times \text{Valence}}{\text{M}} \quad (3.8)$$

Where M = molecular mass

Then the CBE is calculated using the formula:

$$\text{CBE} = \frac{\text{TextRun Cation} - \text{TextRun Anion}}{\text{TextRun Cation} + \text{TextRun Anion}} * 100$$

(3.9)

When the CBE is greater than 5% it indicated that the quality of the data was poor or the water was very acidic while less than 5% showed that the data was good (Hounslow, 1995). According to Hounslow (1995) a solution must be electrically neutral, i.e. the sum of cation in meq/l should equal the sum of the anion. The hydrochemical data from the laboratory analysis were less than 5%.

To assess water quality for irrigation, there are various criteria like TDS or EC, sodium adsorption ratio (SAR), sodium percentage (Na%), and residual sodium carbonate that can be used (Michael 1992; Raghunath 1987).

Sodium hazard in irrigation water is evaluated from the relationship:

$$SAR = \frac{Na^+}{\frac{Ca^{2+} + Mg^{2+}}{2}} \quad (3.10)$$

The sodium percentage was also calculated by the relationship

$$Na\% = \frac{Na^+}{Na^+ + K^+ + Ca^{2+} + Mg^{2+}} * 100 \quad (3.11)$$

Gupta (1983) expressed residual sodium carbonate (RSC) as:

$$RSC = (HCO_3^- - Ca^{2+}) - (Ca^{2+} + Mg^{2+}) \quad (3.12)$$

Permeability index according to Doneen (1964) is expressed as

$$PI = \frac{Na^+ + HCO_3^-}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} * 100 \quad (3.13)$$

$$MH = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} * 100 \quad (3.14)$$

The ratio between major ions were also calculated using excel spreadsheet. Computer software SPSS version 17 (SPSS, 2008), Microsoft Excel spreadsheet, and other statistical package were used in processing the data. Descriptive statistics such as minimum, median and mean were also generated.

3.4.2 Graphical Method

Graphical methods are mostly used to represent the concentration of various parameter and compare the proportion of major ions in water samples (Fetter, 1994). Various graphical method used in this study include Piper trilinear diagram, Gibbs diagram and compositional diagram.

The Piper trilinear diagram was created using groundwater chart programme which plot the relative concentration of major ions in meq/l expressed as percentage on cation and anion triangles and than projected to a point on a diamond shape quadrilateral field. The classification of water is based on the dominant cation and anion occurring at a percentage greater then 50% meq/l. In the case where there is no one cation and anion constituting more than 50% meq/l of the total ions such water is classified as mixed types and is identified by all the important cations and anion (Hem, 1989).

Gibbs diagram (Gibbs, 1970) also highlights the natural evolutionary trends and the possible sources of variation in groundwater hydrochemistry in the area based on the relationship of TDS plot against the weight of $(\text{Na}^++\text{K}/\text{Ca}^{2+}+\text{Mg}^{2+}+\text{N}^++\text{K}^+)$. The diagram is divided into three portions, rock dominance, evaporation-crystallization, and precipitation dominance. Compositional diagrams are generated using excel to plot a pair of measured parameters in an x-y axis. These give various patterns that can be used to explain the relation between such parameters and also their sources.

3.4.3 Statistical methods

Hierarchical Cluster Analysis (CA), and Principal Component Analysis (PCA) are the two main statistical methods employed in these studies. These methods are widely used to reduce the complexity of large-scale datasets and show the relationship between the data components (Mencio and Mass-Palau, 2008). Cluster analysis primarily classifies variables or samples with high similarity into a cluster to minimize their sample number (Massart and Kaufmann, 1983).

In the study, HCA was applied for the grouping of fifty different samples using Ward's linkage method (Ward, 1963) and a classification scheme using Euclidean distance for similarity measurement. Ward method produces the most distinctive groups where each member of each group is more similar to its fellow member than to any member outside the group (Gular et al., 2002).

PCA on the other hand, was conducted using Ca, Mg, K, Na, HCO_3 , Cl, SO_4 , NO_3 , Electrical conductivity, pH, TDS, Total hardness using the Kaiser criterion to extract

various principal components. Component with eigen values greater than or equal to 1 were considered as a possible variance in the study.

Ionic ratios (bivariate plots) are plotted among pairs of related chemical species such as Ca/Mg, Na/Cl, Ca/HCO₃ using excel. The ratios between major ions were employed to determine the variable dependency and the relationships between a variable pair in the water.

CHAPTER FOUR

RESULT AND DISCUSSION

4.0 Introduction

In this chapter, the statistical summary of various physico-chemical parameters of groundwater and dam water samples are presented and discussed. Results and graphs were interpreted and compared with relevant literature. The discussions were categorized in three groups which are summarized below:

1. Water quality: where various parameters that affect human health and aesthetic quality were compared with world health organisation (WHO, 2014) guideline for domestic water use. Also SAR and Wilcoxs diagrams were be used to classify both groundwater and dam water and determine their suitability for irrigation.
2. Water facies and hydrochemistry: involved classifying water into hydrochemical facies and determining the hydrochemical processes that influenced the composition of the water in the area.
3. Stable isotopes were used to determine the origin of water in the study area

and also identified the relationship between groundwater and surface water.

4.1 HYDROCHEMICAL ANALYSIS AND EVALUATION OF WATER QUALITY

The quality of water for an intended purpose depends on the physico-chemical characteristics of the water. This physico-chemical parameter depends on the composition of the host rock, interaction between soil and water and the residence time within the aquifer (Appelo and Postma, 2005). The quality of water in an aquifer is mainly influenced by physical, chemical and biological property. Whereas water with low mineral concentration can be used for multi-purposes such as domestic and irrigation water supply, high concentration of minerals in water may limit its usage.

4.1.1 Domestic Water Quality Assessment

In recent times much importance is placed on the assessment of the quality of groundwater due to its increasing usage. The suitability of the waters for domestic use is determined by comparing the concentrations of the chemical and physical constituents with the WHO (2014) guideline values. This method has been used by Anim et al. (2014) to assess drinking water quality of groundwater in Bunpkurugu yunyo. The detailed result of the analyses of the physico-chemical parameters of both groundwater and surface water with WHO. (2014) guideline values are presented in Table 4.1a and 4.1b respectively.

Table 4.1 a: Statistical summary of physicochemical data of groundwater

Parameter	Unity	Minimum	Maximum	Mean	WHO limit (2014)
EC	uS/cm	192.00	694.00	385.70	1500
Temperature	°C	30.00	36.00	32.10	15
pH		5.96	7.01	6.48	6.5-8.5
TDS	mg/l	96.00	347.00	191.50	500
Sodium	mg/l	8.90	18.60	13.25	200
Potassium	mg/l	0.40	2.00	1.09	12
Calcium	mg/l	15.23	59.32	29.77	72
Magnesium	mg/l	6.80	44.66	22.44	50
Chloride	mg/l	10.00	75.98	21.01	250
Hardness	mg/l	52.00	360.00	168.60	500
Alkalinity	mg/l	18.60	224.00	130.28	1000
Bicarbonate	mg/l	63.44	273.28	148.25	500
Nitrate	mg/l	0.19	7.21	2.42	45
Sulphate	mg/l	15.00	96.13	47.02	250
Fluoride	mg/l	0.44	1.64	1.44	0.5-1.5

Table 4.1 b: Statistical summary of physicochemical data of surface water

Parameter	Unity	Minimum	Maximum	Mean	WHO
Temperature	°C	25.80	28.10	27.26	15
pH		7.11	7.48	7.38	6.5-8.5
EC	uS/cm	21.0	37.0	29.00	1500
TDS	mg/l	60.70	70.80	44.82	500
Hardness	mg/l	40.00	69.00	52.43	
Alkalinity	mg/l	46.00	58.00	51.65	
Sodium	mg/l	3.40	4.80	3.77	200
Potassium	mg/l	1.60	6.70	3.27	12
Calcium	mg/l	4.81	12.81	8.92	72
Magnesium	mg/l	8.25	13.60	10.66	50
Chloride	mg/l	2.00	10.00	4.71	250
Bicarbonate	mg/l	56.12	68.76	62.60	500
Nitrate	mg/l	.06	2.17	.6409	45
Sulphate	mg/l	12.74	32.65	25.09	250

The pH values of water express its tendency to accept or donate hydrogen ions. Studies indicate that the concentration of pH is controlled by the presence of dissolved carbon dioxide, organic matter, ferrous ions, oxidation of sulfur species and

respiration of plant root (Langmuir, 1997). The pH has an influence on many biological, physical, and chemical processes within water bodies (Chapman, 1992).

The pH values in the study range between 5.96 mg/l and 7.01 mg/l with a mean value of 6.48 mg/l, which classify groundwater as slightly acidic to neutral. The surface water showed slightly alkaline in nature with a pH range between 7.11 mg/l and 7.48 mg/l and a mean value of 7.38 mg/l. The WHO, 2014 allowable limit of pH is 6.5 –8.5 and the pH of the water in the study is within the limit for drinking.

The TDS values of the surface water ranged from 60.70 mg/l to 70.80 mg/l with a mean value of 44.8 mg/l and for groundwater it was from 96 mg/l to 347 mg/l with a mean of 91 mg/l. Generally water with low value of TDS below 1000 mg/l could be as a result of slow weathering processes of rocks, low residence times or continuous recharge from rainfall which causes significant dilution (Chapman, 1996). The study area is mainly underline by granitic rocks which have high resistivity to weathering and therefore will dissolve slowly. Minerals such as carbonate as well as halite, gypsum react faster in contact with water and attain equilibrium in a short time as compared with silicate minerals which are very slow, especially in very low temperature.

Classifying water based on its TDS content, with reference to Freeze and Cherry (1979) classification scheme (Table 4.2) showed that, both surface water and ground water from the study area fell within the fresh water type category and therefore could be used for domestic purpose.

Table 4.2: Classification of water based on TDS after Freeze and Cherry (1979)

TDS(mg/l)	Class
<1000	Fresh water type
1000-10000	Brackish water type
10000-100000	Saline water type
>100000	Brine water type

The relationship between two variables can be assessed using correlation coefficient. It is a simple measure to show how well one variable can be used to predict the other (Bahar and Reza, 2010). The TDS of groundwater is directly proportional to the measured EC, therefore a measurement of TDS is an indirect measurement of EC. A plot of EC against TDS (Fig. 4.1) showed a strong correlation between TDS and EC with a correlation coefficient of 0.999. Therefore the high values of TDS justify the high values of EC recorded.

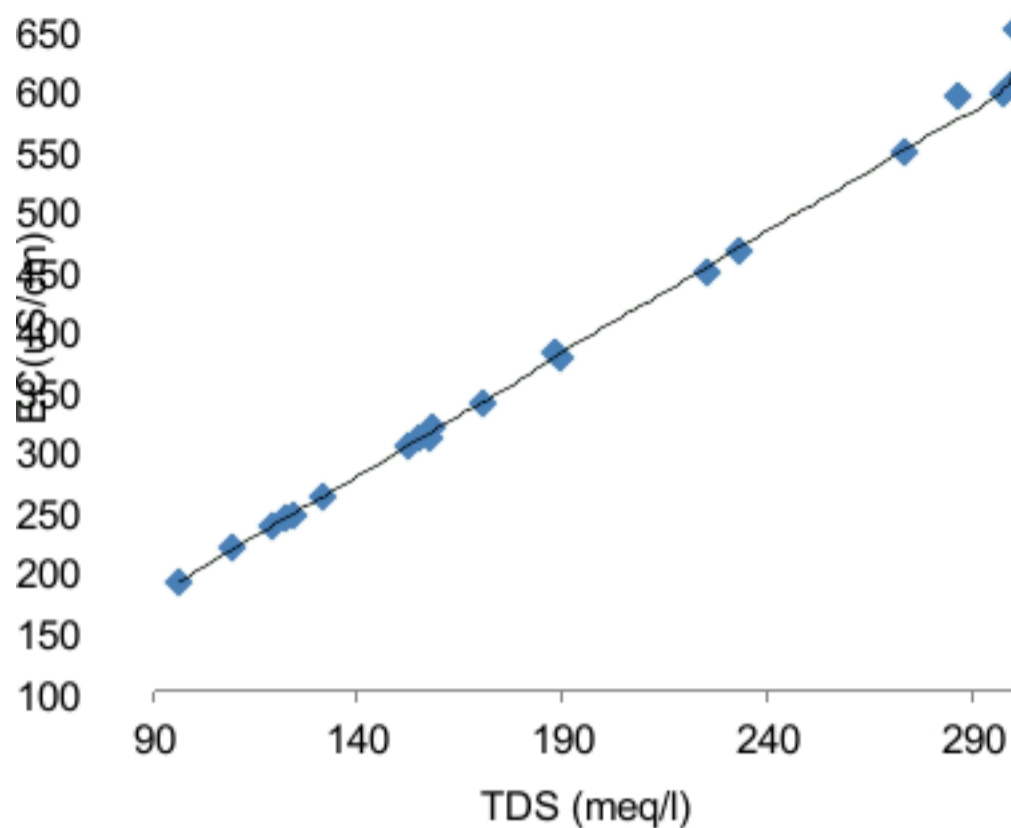


Fig. 4.1: A plot of EC against TDS of groundwater in the study area.

EC shows the degree of mineralization of the water and the capacity to convey electrical current. Intake of water with high EC may cause stomach irritation in a human being (Singh et al., 2008). Hence it is important that the EC value is within WHO, 2014 value of 1500 $\mu\text{S}/\text{cm}$. Water can be classified as type I, if the value is less than 1,500 $\mu\text{S}/\text{cm}$, type II, if the value EC is ranges between 1,500 $\mu\text{S}/\text{cm}$ and 3,000 $\mu\text{S}/\text{cm}$ and type III, if the value is above 3,000 $\mu\text{S}/\text{cm}$ (Sarath-Prasanth et al., 2012).

The electrical conductivity of groundwater ranged from 192 $\mu\text{S}/\text{cm}$ to 694 $\mu\text{S}/\text{cm}$ with a mean value of 385 $\mu\text{S}/\text{cm}$ and surface water ranged from 21 $\mu\text{S}/\text{cm}$ to 37 $\mu\text{S}/\text{cm}$ with a mean of 29 $\mu\text{S}/\text{cm}$. Therefore most of the groundwater and all the surface water were classified as type I with only a few of the groundwater samples falling under type II. EC showed positive correlation with magnesium, calcium, bicarbonate ions and to some extent chloride as sow in table 4.4. This implied that water would have high conductivity if most of these ions were release from the host during chemical

reaction. Both water bodies had EC within the WHO (2014) limit of 1500.

The values of total hardness which is a measure of the total sum of the concentrations of calcium, magnesium, bicarbonate and carbonate ranges from 52 mg/l to 360 mg/l and a mean of 168 mg/l for groundwater while that of surface water ranges from 43 mg/l to 45 mg/l with a mean of 44.8 mg/l. All values were within the WHO (2014) recommended allowable limit of 500 mg/l for drinking.

Hardness of water is in two forms; permanent hardness and the temporary hardness. The temporal hardness occurs when calcium and magnesium combine with bicarbonate and carbonate ions whiles the permanent hardness occur when calcium and magnesium combine with sulphate, chloride and nitrate ions (Driscoll, 1989).

Table 4.3: Classification of water based on hardness (Brown et al.,1970)

Hardness(mg/l)	Class	% of sample
0-63	Soft	0
64-120	Moderately hard	12
121-180	Hard	88
>180	Very hard	0

To classify water using total hardness Brown et al., (1970) classification was used (Table 3.4). About 12% of the groundwater samples and 100% of the surface water samples fell within the moderately hard type of water while 88% of the groundwater samples fell as hard type of water (Table 3.4). The intake of hard water for a very long time may cause illness such as anencephaly, cardiovascular disorders and some types

of cancer, (Davy et al. 1991; Agrawal and Jagetia, 1997). The lithology is made up of granite, sandstone and conglomerate which consist of considerable amount of carbonate mineral and silicate, hence the weathering of these rocks will release appreciable amount of calcium and magnesium and when combine with bicarbonate or sulphate causes water hardness.

The respective minimum and maximum temperature obtained from groundwater are 30°C and 36°C and a mean value of 32.1°C. The temperature of the surface water also varies from 25.8°C to 28.1°C with a mean of 27.0°C. All values of physical parameters (pH, EC, TDS, Total hardness, Temperature) were within the WHO (2014) recommended allowable limit for drinking water.

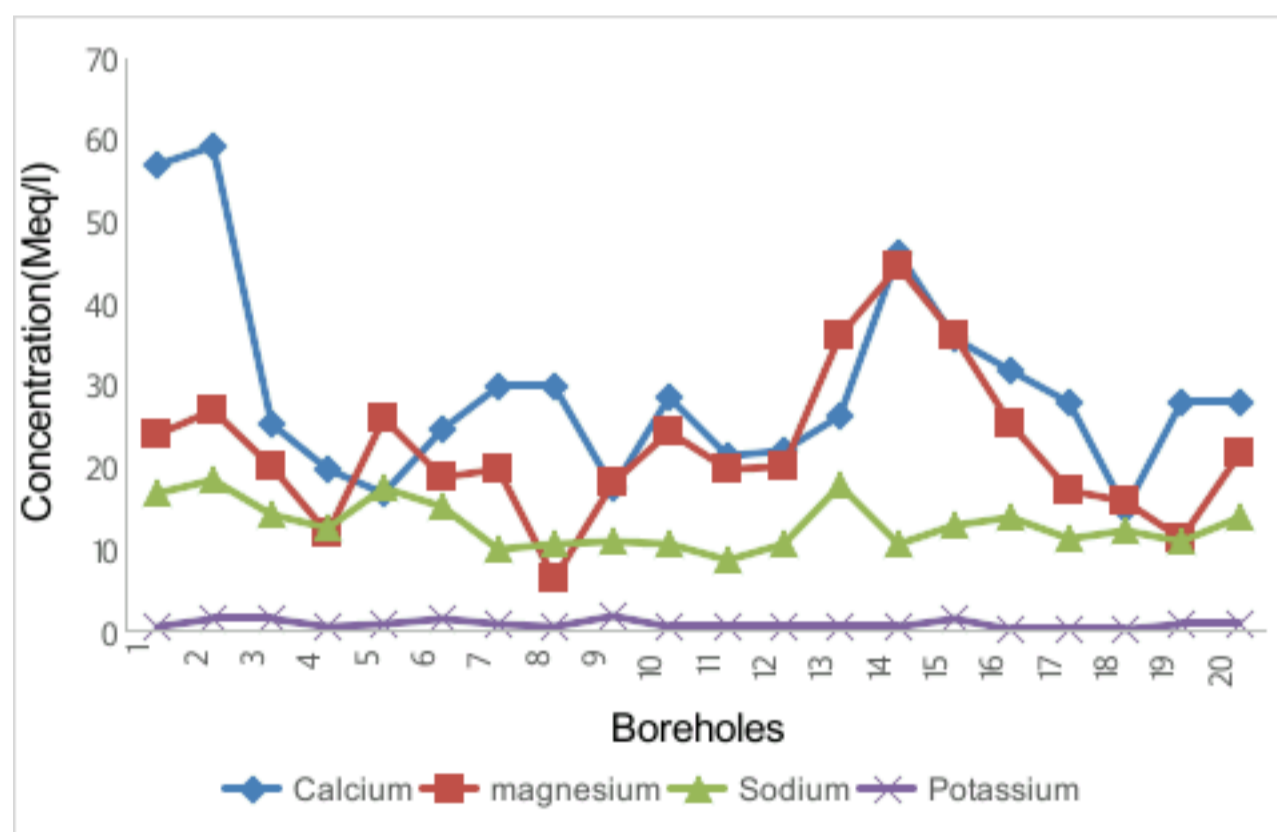


Fig.4.2 a: Showing major cation dominance pattern in groundwater.

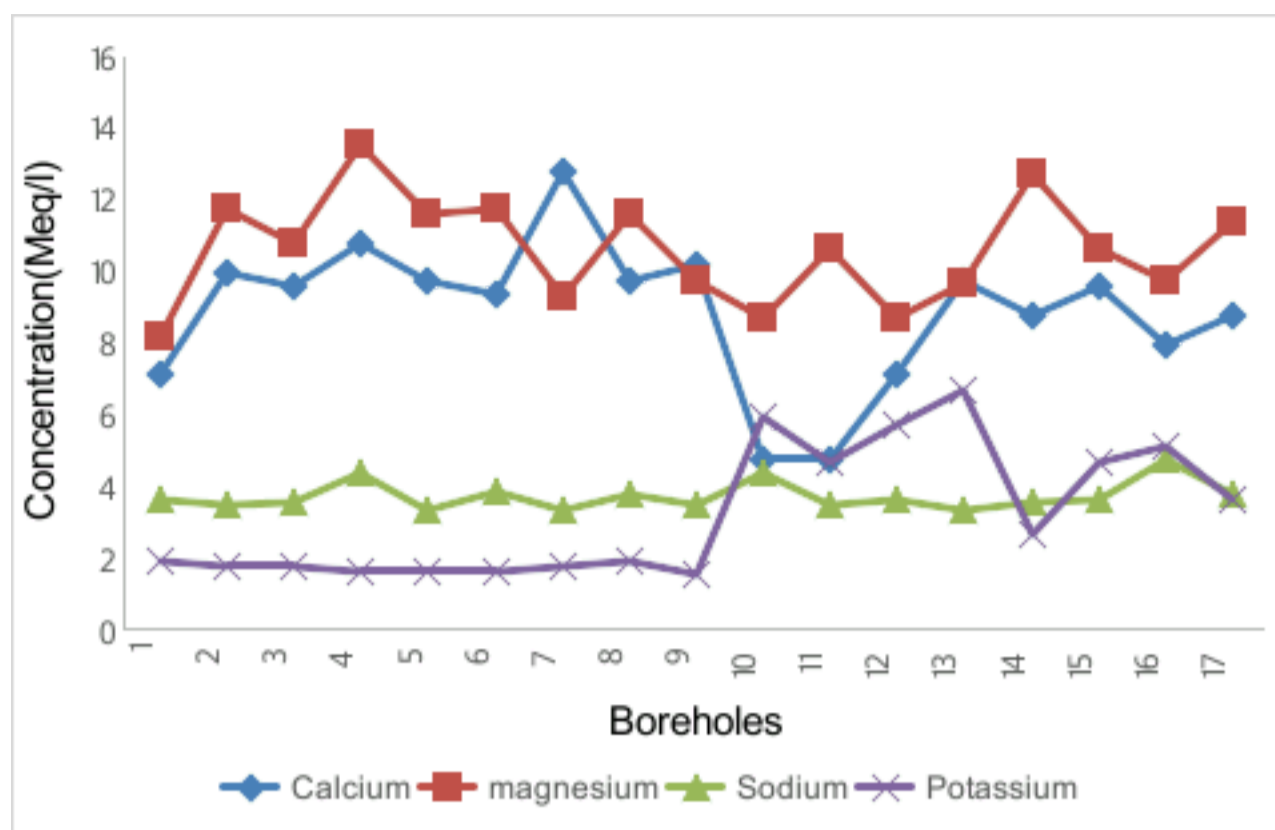


Fig. 4.2 b: Showing major cation dominance pattern in surface water.

The calcium concentration in groundwater ranges from 15.23 mg/l to 59.32 mg/l with an average of 29.77 mg/l and that of surface water is 4.8 mg/l to 12.8 mg/l with a mean of 8.9 mg/l (Table 4.1) and is within the WHO, 2014 standard. Major cations concentrations from the analyses of both groundwater and surface water generally show a trend of Ca^{2+} Mg^{2+} Na^+ K^+ in terms of dominance (Fig 4.2 a and b). The general relative abundance of calcium composition in groundwater can be derived from the chemical weathering of Ca-feldspars, plagioclase-rich rock origin and also some sedimentary carbonate minerals like (Kirchner, 2003). Therefore the concentration of calcium in the water from the area may originate from the granitic terrain.

The source of magnesium concentration in groundwater is due the leaching of magnesium bearing minerals like silicate minerals. Biotite, Ca-plagioclase,

hornblende pyroxenes are the compositions of granitic rocks (Chapelle, 1983; Fetter, 1994) which when dissolved to release magnesium into the water. They are also found in some carbonate minerals. The geology of the study is mainly granitic rocks and therefore will dissolve slowly to release magnesium into water. The maximum and minimum range of magnesium values are 6.8 mg/l to 44.66 mg/l with a mean value of 22.4 mg/l for groundwater and that of surface water is 13.6 mg/l to 8.25 mg/l and an average of 10.66 mg/l (Table 1.4 a and b) and were within the WHO (2014) limit for drinking.

The range of sodium concentration is from 8.9 mg/l to 18.6 mg/l for groundwater with the mean of 13.25 mg/l and that of surface water is 3.4 to 4.8 mg/l with a mean of 3.7 mg/l. Among the alkali metals sodium is the most abundant in groundwater and it is naturally mobile and highly soluble. Sodium concentration in water can be from the dissolution of sodium plagioclase minerals from granitic rock, dissolution of soil salts, evaporation, ion exchange and human activities such as waste disposal and industrial waste waters (Subramani et al., 2005). The relative high values of sodium as compare to potassium may due to the addition of sodium by ion exchange process. The ranges of sodium concentration are with WHO (2014) limit for drinking. Illness such as nausea, vomiting, convulsions, muscular rigidity, and cerebra may result due to the intake of highly concentrated sodium water (Elton et al., 1963).

The relatively less concentration of potassium compared to sodium can be attributed to its lesser mobility and high resistance to weathering of potassium-rich minerals (Chapman, 1992) such as K-feldspar and some micas. Negative health effects of high concentration of potassium in drinking water is not common in human beings since

potassium is rapidly excreted by the kidney and also can cause vomiting (Gosselin et al. 1984). The concentration of potassium recorded in the area for groundwater ranges from 2 to 4 mg/l with a mean of 1.09 mg/l and for surface water ranges from 1.6 to 6 mg/l and an average of 3.27 mg/l. Both waters have potassium concentration within the WHO (2014) limit.

The concentration of cation in water samples is among the general element essential for human health and metabolism and should be available in drinking water at the acceptable concentration. However, if some are above the limit permissible for drinking, the water may not be tolerable and may become hazardous to health. The cations were within the permissible limit for drinking, according to the World Health Organization (2014).

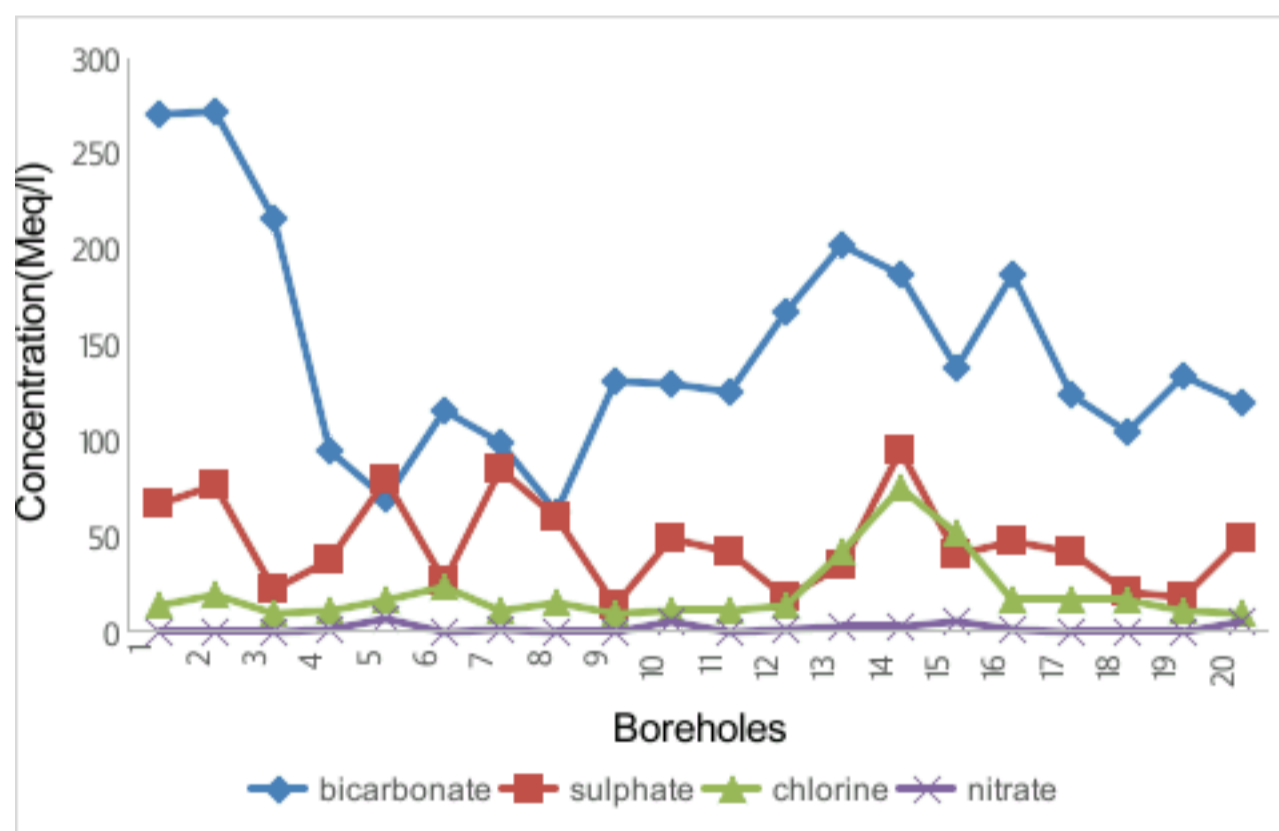


Fig. 4.3 a: Showing major anions dominance trend in groundwater

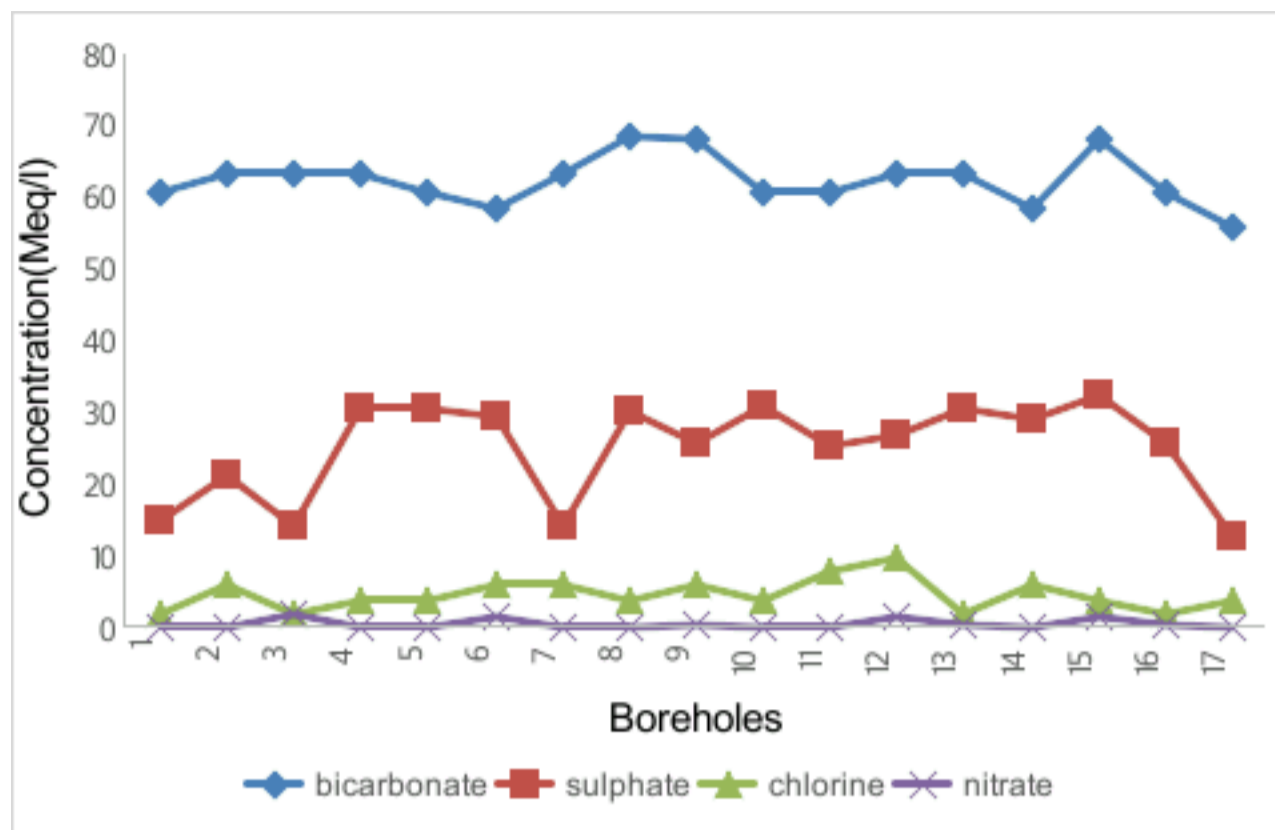


Fig 4.3b: Showing major anion pattern in surface water

Anions concentration in both groundwater and surface water samples indicated that the dominant anion follows the trend of HCO_3^- SO_4^{2-} Cl^- NO_3^- (Fig. 4.3 a and b). Among the anions, preference is given to nitrate, chloride, and sulphate because their concentration may indicate pollution from anthropogenic activities (Bakari et al., 2014). From Table 4.1 nitrate ranges between 0.19 mg/l to 7.21 mg/l with an average of 2.41 mg/l for groundwater and 0.6 mg/l to 2.17 mg/l with a mean of 2.4 mg/l for surface water which is below the permissible limit of 45 mg/l (WHO, 2014).

Nitrate concentration in water is usually as a result of the complete oxidation of nitrogen and mostly used to identify groundwater pollution. Nitrates usually do not originate much from rocks, but occur in water as a result of decay of organic matter, sewage, nitrate fertilizer and nitrate in the soil (Chapman, 1996). Nitrogen plays a dominant role in the life process of plant and animals. When there is decomposition of organic matter through bacterial activities, the complex protein is converted to

ammonia, nitrite and eventually nitrate. The produced nitrate may then leach into the groundwater or surface water bodies. The concentration of nitrate in groundwater and surface water in the area is quite below the recommended limit of 45 mg/l (NO_3^-) for drinking by WHO, 2014. This implies that water in the area was not polluted and therefore safe from nitrate contamination from human activities.

Natural waters have low chloride ions concentration usually less than 10 mg/l unless the water is brackish or saline. Chloride ion in water may be influenced by diverse processes such as weathering of rocks and atmospheric salts, domestic and industrial waste contamination (Driscoll, 1989; Hem, 1989; Sarath, 2012). High concentration of chloride causes corrosion in metal tubes and also give water a salty test when combination with sodium. The concentration of chloride in groundwater ranged from 10 mg/l to 75 mg/l with a mean of 21 mg/l and for surface water recorded 2 mg/l to 10 mg/l with an average of 4.7 mg/l. The low value of chloride may be due to Base Exchange reactions (Freeze and Cherry, 1979).

Sulphate concentration was high as compared to nitrate and chloride. This anion could be contributed by the dissolution of gypsum and anhydrite (CaSO_4). Other source of sulphate is by oxidation of metallic sulphides, pyrite minerals and some anthropogenic activities (Chapman, 1992). The concentration ranged from 15.7 mg/l to 96.65 mg/l with a mean of 47.0 mg/l for groundwater and 12.74 mg/l to 32.65 mg/l with a mean of 25.09 mg/l for surface water. The low values of sulphate can be attributed to the low level of gypsum which is mainly found in sedimentary deposit. The action of sulphur reducing bacteria which aid in the removal of sulphate in a form hydrogen sulphide and escape to the atmosphere as indicated in Freeze and Cherry, 1979. The

sulphate ion concentration in groundwater of the study was below the maximum allowable limit of 250 mg/l in all samples.

Bicarbonate concentrations in groundwater affect the hardness and alkalinity of water. It is derived from carbon dioxide in the atmosphere, dissolution of carbonate minerals such as calcite and dolomite (Chapman, 1992). Reaction of water with atmospheric carbon dioxide or carbon dioxide from decomposed organic matter produces bicarbonate and acid. Granitic rock that is made of plagioclase feldspar, quartz, potassium feldspars, hornblende and biotite can also release bicarbonate into water during chemical reaction (Appelo and Poatma, 2005). The concentration of bicarbonates in groundwater from the area ranges from 63.44 mg/l to 274.2 mg/l with a mean value of 148.2 mg/l and surface water ranges from 56.2 mg/l to 67.6 mg/l and a mean of 62.59 mg/l and all samples were within the WHO, 2014 allowable limit for drinking.

The concentration of fluoride ranged from 0.4 mg/l to 1.64 mg/l with a mean of 1.4 mg/l. According to WHO (2012) Fluoride is an essential mineral for healthy bones and teeth however, very high fluoride concentrations can lead to skeletal and dental fluorosis (Baird, 1999). Fluoride in groundwater in the study area is associated with the dissolution of fluoride-containing minerals known as fluorite (CaF_2) which is associated with the bongo type granite (e.g. Apambire et al., 1997).

All the major anion concentrations were within the WHO (2014) limit except a few samples had fluoride concentration above the guideline value therefore generally, groundwater and damp water within the catchment area is safe for drinking.

The major ions that contribute to groundwater chemical budget according to Chitradevi and Sridhar (2011) are Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- , and SO_4^{2-} . From Table 4.4 it is revealed that Ca^{2+} , Mg^{2+} , and Cl^- produce high correlation co-efficient (very strong relationship and linearity) with TDS. On the other hand HCO_3^- , Na^+ , K^+ and SO_4^{2-} indicated a relatively weak linear relationship with TDS. Therefore the high correlation coefficient shown in Table 4.4 between TDS and Ca^{2+} , Mg^{2+} and Cl^- depicts that the dissolution of these chemical contribute to the high value of TDS.

Table 4.4: Correlation matrix of groundwater chemistry in the study area

	EC	PH	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	NO_2^-	SO_4^{2-}	F^-
EC	1											
Ph	.304	1										
TDS	.999	.320	1									
Na^+	.443	.449	.446	1								
K^+	.013	.258	.018	.244	1							
Ca^{2+}	.718	.341	.709	.333	.001	1						
Mg^{2+}	.694	.168	.700	.026	-.120	.243	1					
Cl^-	.671	-.160	.672	.100	.126	.407*	.443	1				
HCO_3^-	.586	.723	.591	.538	.253	.600	.438	.072	1			
NO_3^-	.289	-.316	.283	-.144	-.269	-.075	.333	.263	-.424	1		
SO_4^{2-}	.510	.011	.502	.242	-.296	.597	.206	.423	.017	.382	1	
F^-	.223	-.520	.203	-.079	-.481	.286	-.037	.375	-.225	.348	.330	1

4.1.2 Suitability of Water for Irrigation Use

The quality of water, the type of soil, and the type of crops to be cultivated play an important role for suitable irrigational practices. The chemical composition of

dissolved ions in irrigation water affect its quality there by affecting plants and the agricultural soil both physically and chemically thus reducing crops productivity and the soil structure. The major effect of these ions is that, they increase the osmotic pressure in the soil solution thus preventing water from being adsorbed by the plant root causing plant to wilt. The chemical effect is to disrupt plant metabolism (Thiyagarajan et al., 2011).

Therefore, the suitability of groundwater for irrigation can be assessed by comparing sodium concentration to the concentration of the total cations in the water (Prasanth et al., 2012). Hence irrigation water suitability is mainly based on the estimation of the concentration of parameters like salinity, sodium, bicarbonate hazard concentrations, Permeability Index (PI), and magnesium hazards.

Sodium Adsorption Ratio (SAR) evaluates the ratio of sodium content to calcium and magnesium concentration. SAR value is used to calculate the degree to which sodium in irrigation water tends to enter into ion exchange with calcium and magnesium in the soil. Calcium and magnesium in the right proportions can act as a buffer to the effect of sodium in the soil. High values of SAR means that calcium and magnesium in water will be replaced by sodium increasing the concentration of sodium whereas low values of SAR implies there is a greater proportion of calcium and magnesium as compared to sodium. Water with high sodium adsorption ratio when used for irrigation affects the permeability of soil. Sodium-Adsorption Ratios for groundwater and damp water samples of the study area were less than 10 which indicate excellent quality for irrigation (Table 4.5) using the USSL (1954) classification scheme.

Table 4.5: EC and sodium hazard for irrigation water (USSL, 1954)

Water class	Electrical conductivity	SAR
Excellent	<250	Up to 10
Good	250 –750	10-18
Fair	750 –2250	18-26
Poor	>2250	>26

Electrical conductivity is a good measure of salinization. The osmotic pressure of the soil solution increases when there is high salt concentration in water resulting in a drought condition. Even though plenty of moisture may appear to be in the field, the plants wilt because less water is absorbed by the roots. Based on the classification of ground water using electrical conductivity, there are four major classes (Table 4.5). Most of the samples fall between the ranges of 250-750 us/cm indicating that water is good for irrigation use and a few of the samples belong to the excellent class of water types.

Hem (1989) noted that when electric conductivity combines with SAR it can be used to measure the suitability of water for irrigation. Therefore EC values were plotted against SAR on the US salinity diagram (USSL., 1954) (Figure 4.4). It illustrates that almost 50% of the samples fall on C1-S1 classes meaning low salinity and low sodium water, and 50% of samples fall in C2-S1 classes, indicating medium salinity to low sodicity. These water types are suitable for almost all types of crops production and all soil types and the potential of this class of irrigation water to cause infiltration problem is improbable. The dam water was also classified under C1-S1 category and can be used for all types of crop under all soil types.

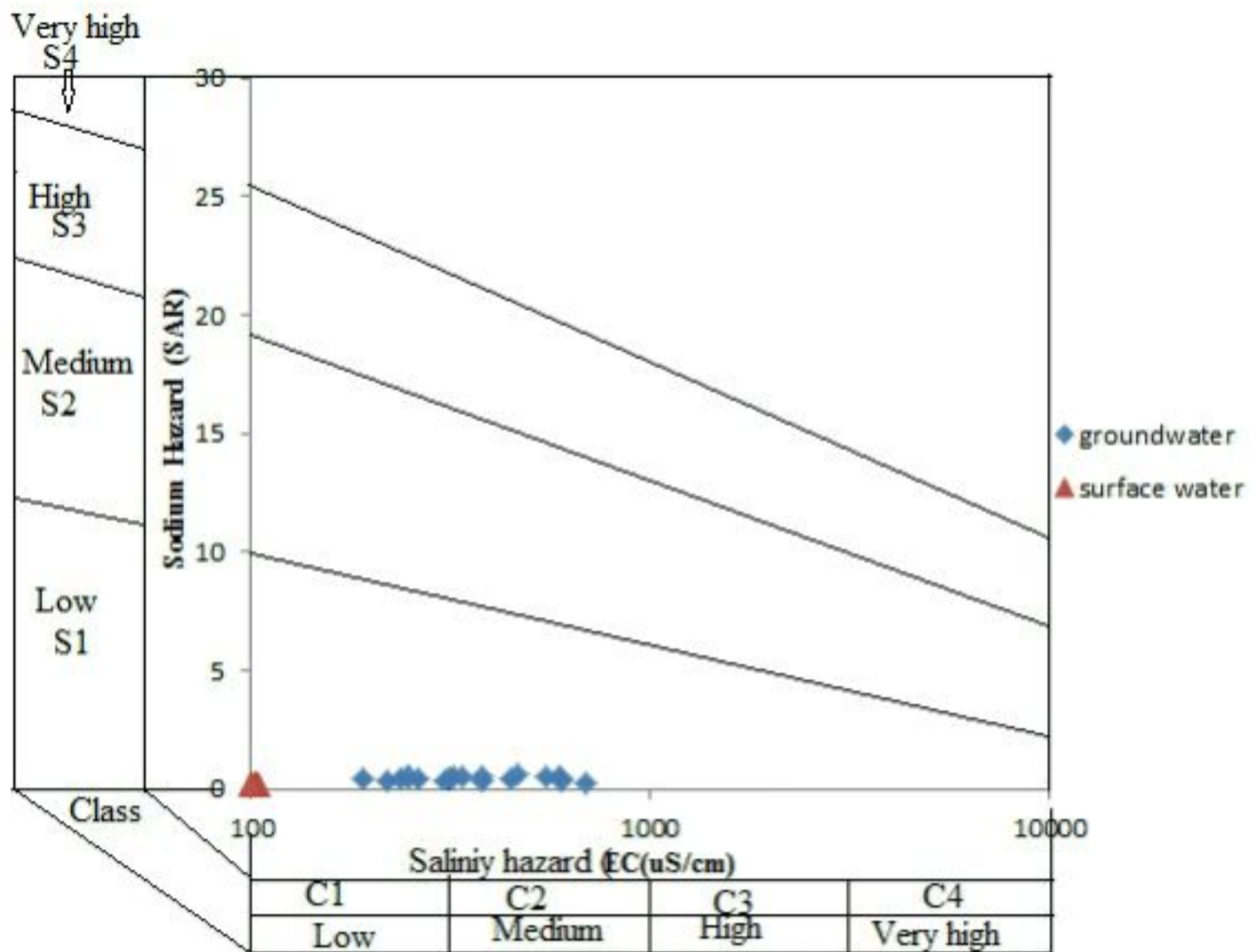


Fig. 4.4: US salinity laboratory S diagram of the study area.

The percentage of sodium content in groundwater also affects irrigation water this is defined by Equation 3.11. Calculated sodium percentages in the study ranges between 8% and 22% for groundwater and that of the surface water range between 11% to 27%. Wilcox (1955) plotted percent sodium and electric conductivity to classified groundwater for irrigation purposes. The diagram (Fig. 4.5) show that all the groundwater samples and the dam water samples fell within excellent to good category, which classifies water suitable for irrigation.

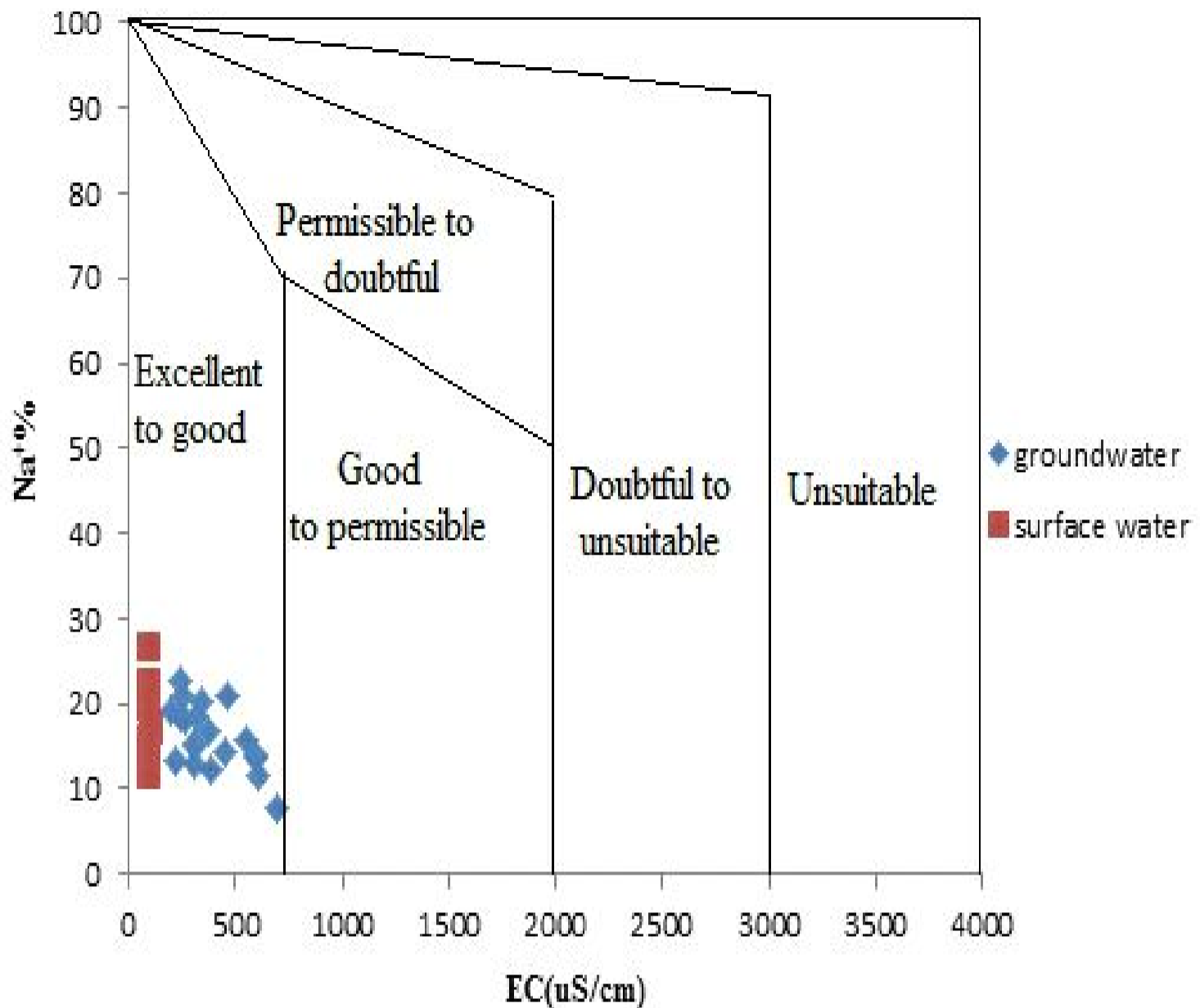


Fig. 4.5: Wilcox δ diagram for the study area

The concentration of calcium plus magnesium when less than carbonate plus bicarbonate concentration in water is termed 'Residual Sodium Carbonate (RSC). RSC index is calculated to determine the bicarbonate hazards on plants and soils. High RSC can cause stunted growth in plant. If water has a high concentration of bicarbonates there is a possibility for calcium and magnesium to precipitate as calcite raising the content of sodium.

The classification of irrigation water according to the RSC values suggested by Mclean and Jankowski (2000) is that water having less than 1.25 meq/l or equal to

1.25 meq/l of RSC is excellent water for irrigation purpose, whereas, water having RSC values between 1.25 meq/l to 2.5 meq/l is marginally accepted for irrigation purpose and water having more than 2.5 meq/l of RSC is not suitable for irrigation purposes. Based on RSC values calculated and plotted against the samples (Fig. 4.6), all the dam water samples and about 45% of groundwater samples showed values less than 1.25 meq/l thus categorized as excellent for irrigation use. Thirty percent (30%) of the groundwater samples fell within marginal category of irrigation water types and the remaining samples fell above 2.5 meq/l implying that the water is not accepted for irrigation. The continuous use of water with RSC above 2.5 meq/l will cause the calcium and magnesium to precipitate and over time will increase the concentration of sodium.

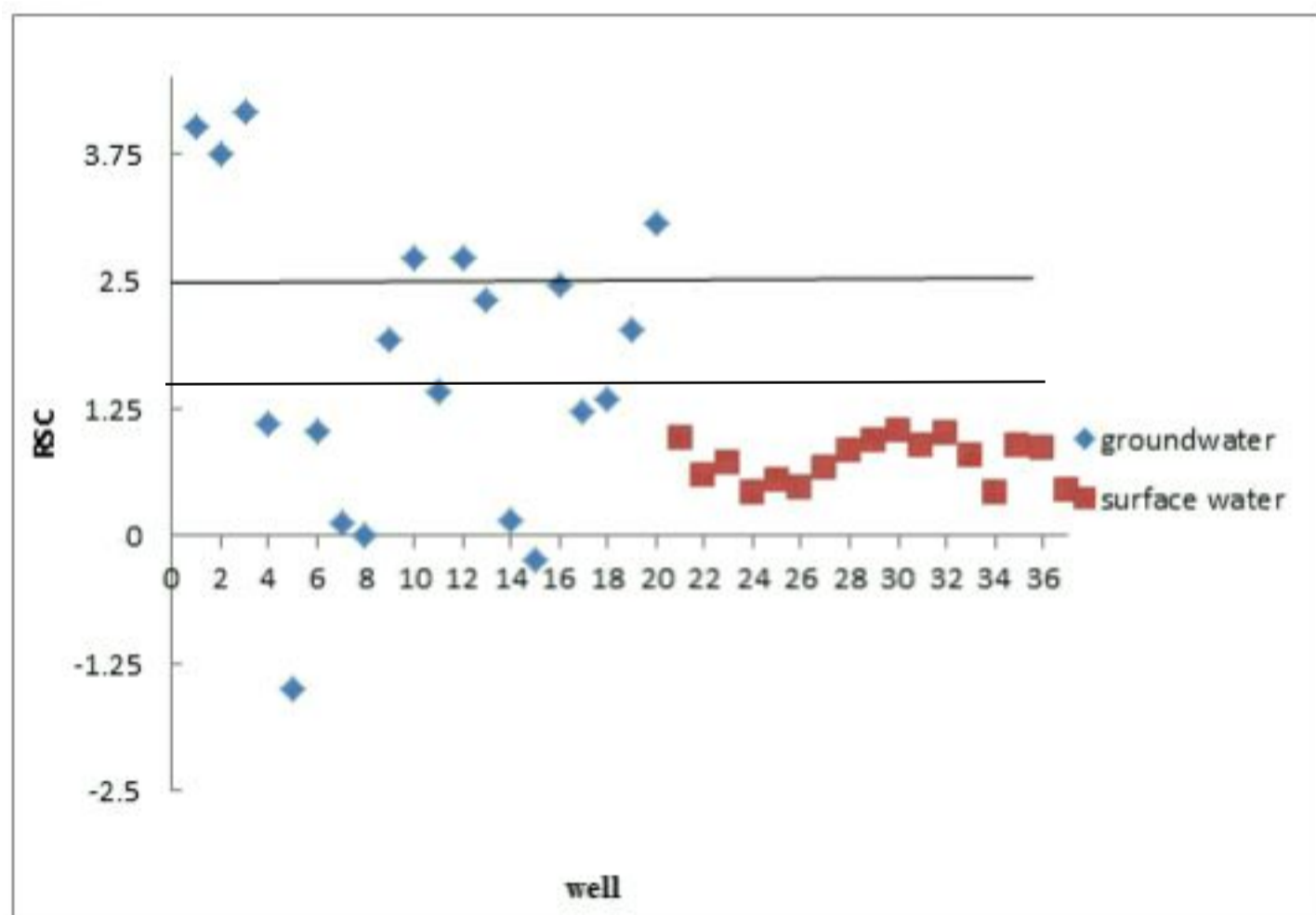


Fig. 4.6: A plot of RSC against wells for the study area.

Permeability Index (PI) values also have an influence on the water suitability for irrigation. The PI values of water measures the collective concentrations of Na^+ and HCO_3^- relative to the total cation content of the water. The soil permeability is affected by long term use of irrigation water influenced by high PI.

Based on PI Doneen (1964) and Rangunath (1987) developed a criterion for assessing the influence of irrigation water on physical properties of soil by plotting calculated PI against total ions (Fig. 4.7). Three irrigation water types were classified; Class I water type shows low PIs values and is the suitable water type for irrigation, Class II is the acceptable type of water and Class III are the unacceptable type of irrigation water with maximum PIs values. From the plot of PI against total ions (Fig. 4.7) some of the groundwater samples fell within the class I indicating good water for irrigation over a long period of time and some of the groundwater and damp water samples fell within class II meaning water is acceptable for use. Also some of the samples for both groundwater and surface water samples fell within class III which is not accepted for irrigation.

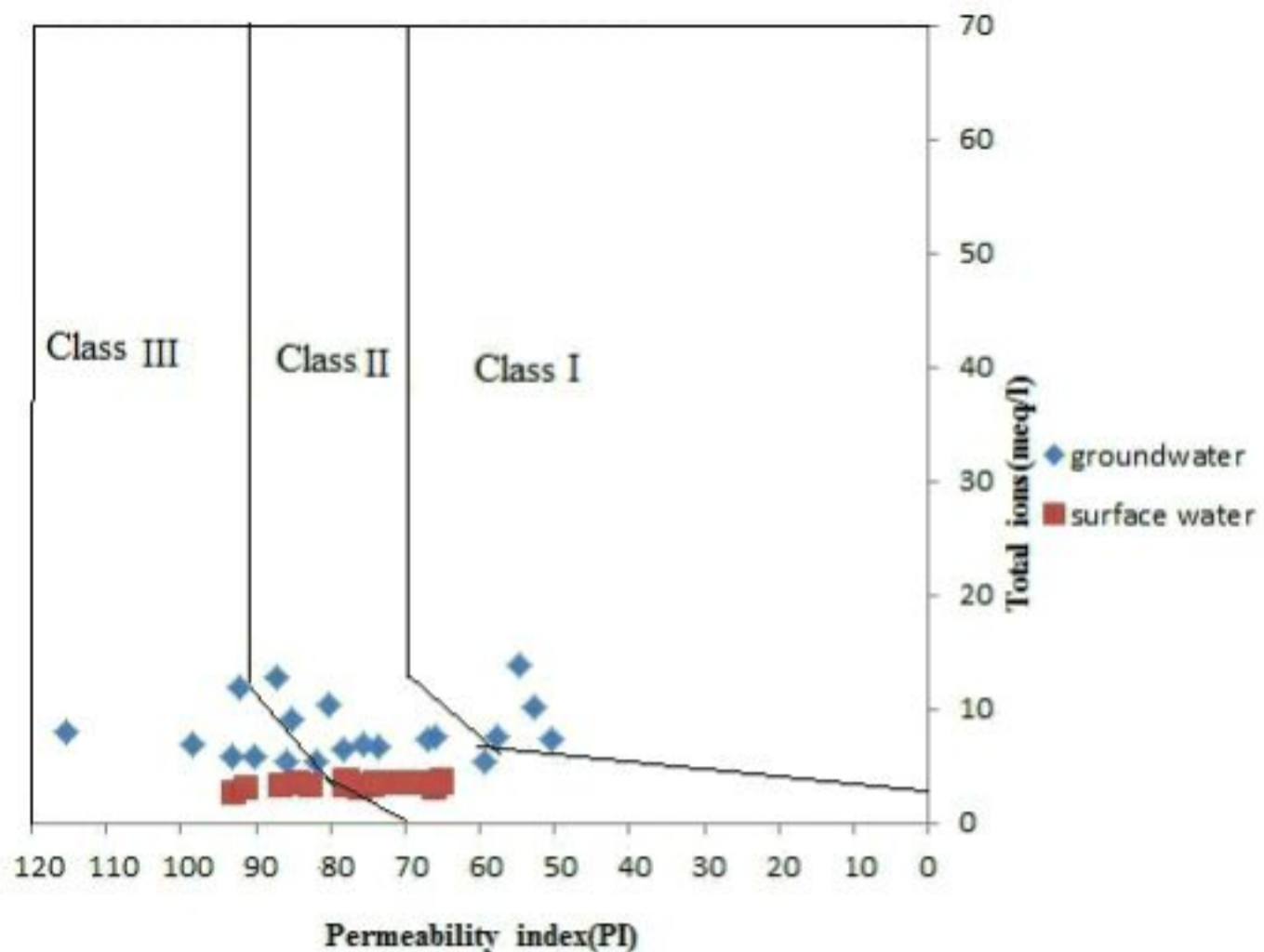


Fig. 4.7: A plot of PI against total ions for the study area.

4.2 MECHANISM CONTROLLING WATER CHEMISTRY

The concentration of various dissolved ions in water is influenced by the geo-environmental conditions. Literature relevant to water characterization explain the relationship of water chemistry and aquifer lithology. From such relationship the origin and distribution of dissolved constituents and factors controlling groundwater chemistry can be deduced.

Gibbs (1970), proposed a method where the natural processes through which groundwater acquire its chemistry such as water-rock interaction, precipitation or evaporation can be identified. Various works, for example Kortasi (2006) and Yidana and Yidana (2010) have used this method to identify the possible sources of water

chemistry. Gibbs diagram (Fig. 4.8) is made by plotting TDS versus $(\text{Na}^+ + \text{K}^+)/(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ for cation and also TDS versus $\text{Cl}/(\text{Cl} + \text{HCO}_3^-)$ for anion and is divided into three portions; precipitation dominance where Na^+ and Cl^- is the major ions, rock-water dominance has high Ca^{2+} and HCO_3^- concentration, and evaporation dominance with high Na^+ and Cl^- . That part of the diagram with high TDS and high $(\text{Na}^+ + \text{K}^+)/(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ ratio is mark by evaporation dominance, while rock dominance mark the zone with moderate TDS and moderate $(\text{Na}^+ + \text{K}^+)/(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ and low TDS and low $(\text{Na}^+ + \text{K}^+)/(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+})$ is mark as rainfall dominance.

The diagram (Fig. 4.8) showed that the groundwater and surface water samples fell in the rock dominance region indicating that the waters acquired their chemistry from rock water interaction. This method of evaluation does not show the signatures of impact of human activities on water chemistry.

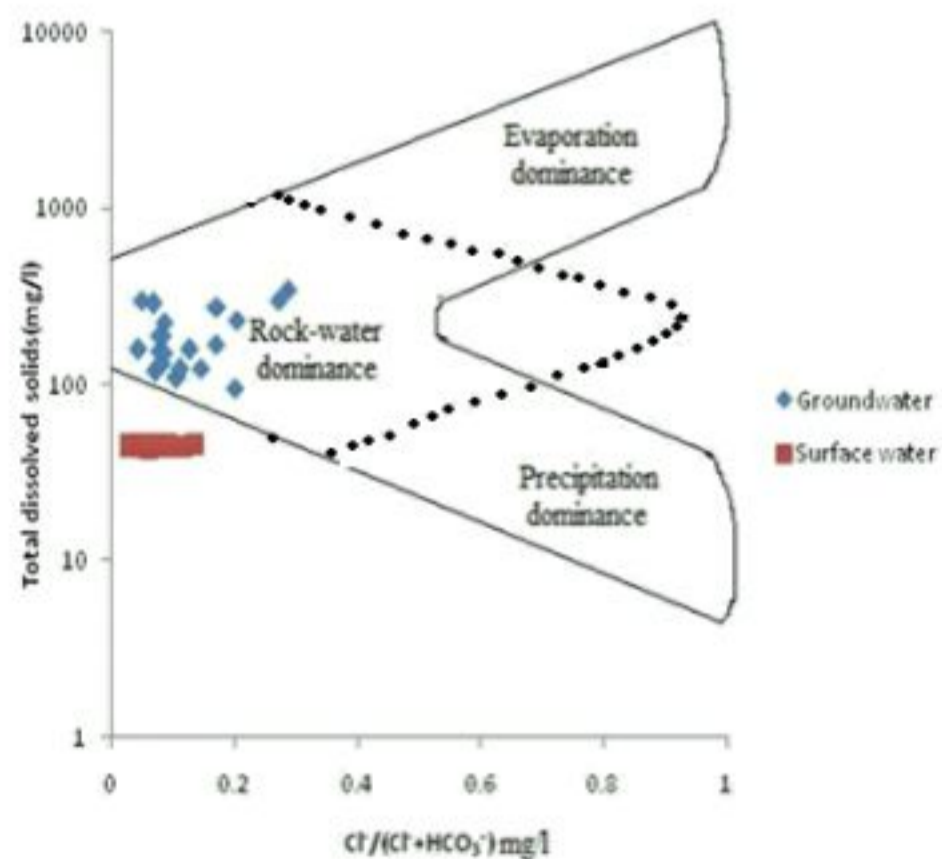


Fig. 4.8 a: Plot of TDS against the ratio of $\text{Cl}/(\text{Cl}+\text{HCO})$ of water samples in the study area

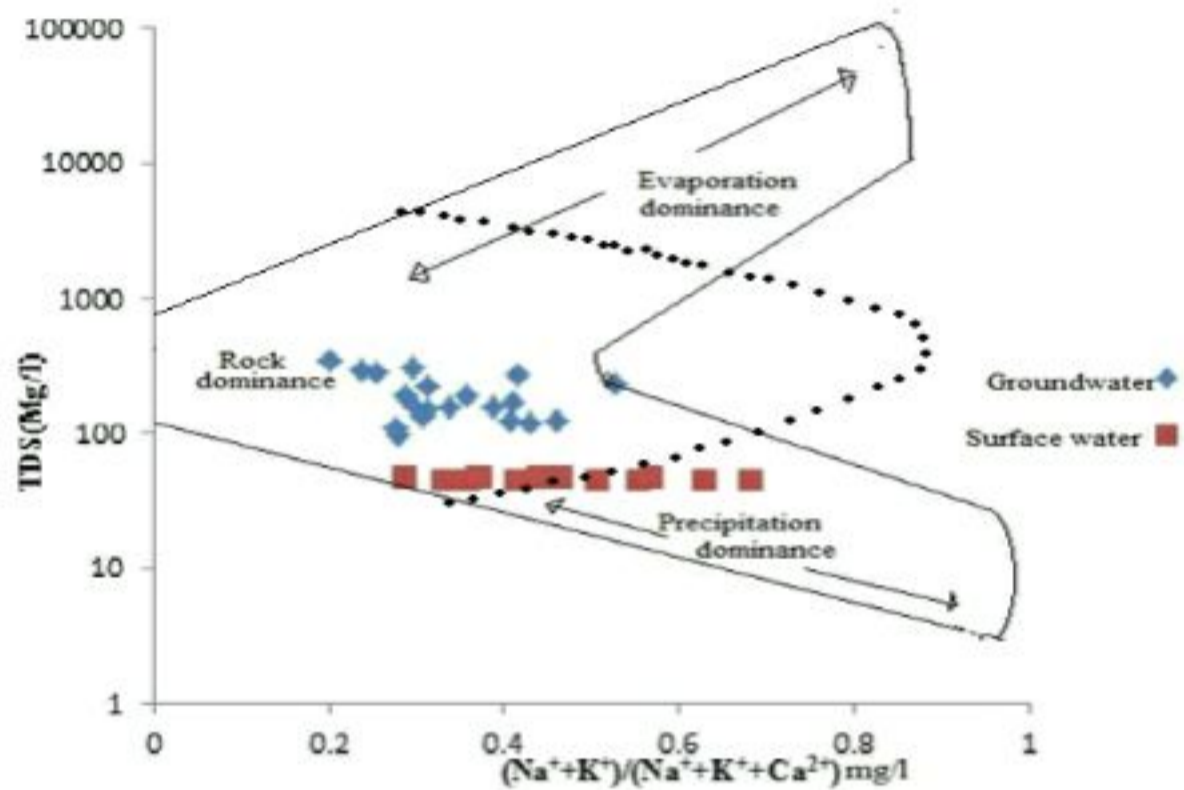


Fig. 4.8 b: Plot of TDS versus the ratio of $\text{Cl}/(\text{Cl}+\text{HCO})$ of water samples in the study area.

4.2.1 Hydrochemical facies

Water analysis usually involves large data set that need sorting and classification into different hydrochemical facies which help to trace the pathways and hydrogeochemical processes of groundwater evolution. The analytical method used includes the Piper trilinear diagram (Fig. 4.9). In this diagram each cation is expressed as a percentage of the total cations in meq/l and plotted in the left triangle while anions are plotted in the right triangle (Piper 1944). Each point is then projected into the diamond shape field and the point where the extension intersects indicates the character of the water. This diagram has been used by several writers to study the hydrogeochemical water type in different parts of the world (Subramani, et al., 2005;

Pandian and Sankar, 2007; Loh et al., 2014; Ganyaglo et al., 2010). Similarities and differences among water samples can be identified by the piper diagram since water of similar chemistry have the same features.

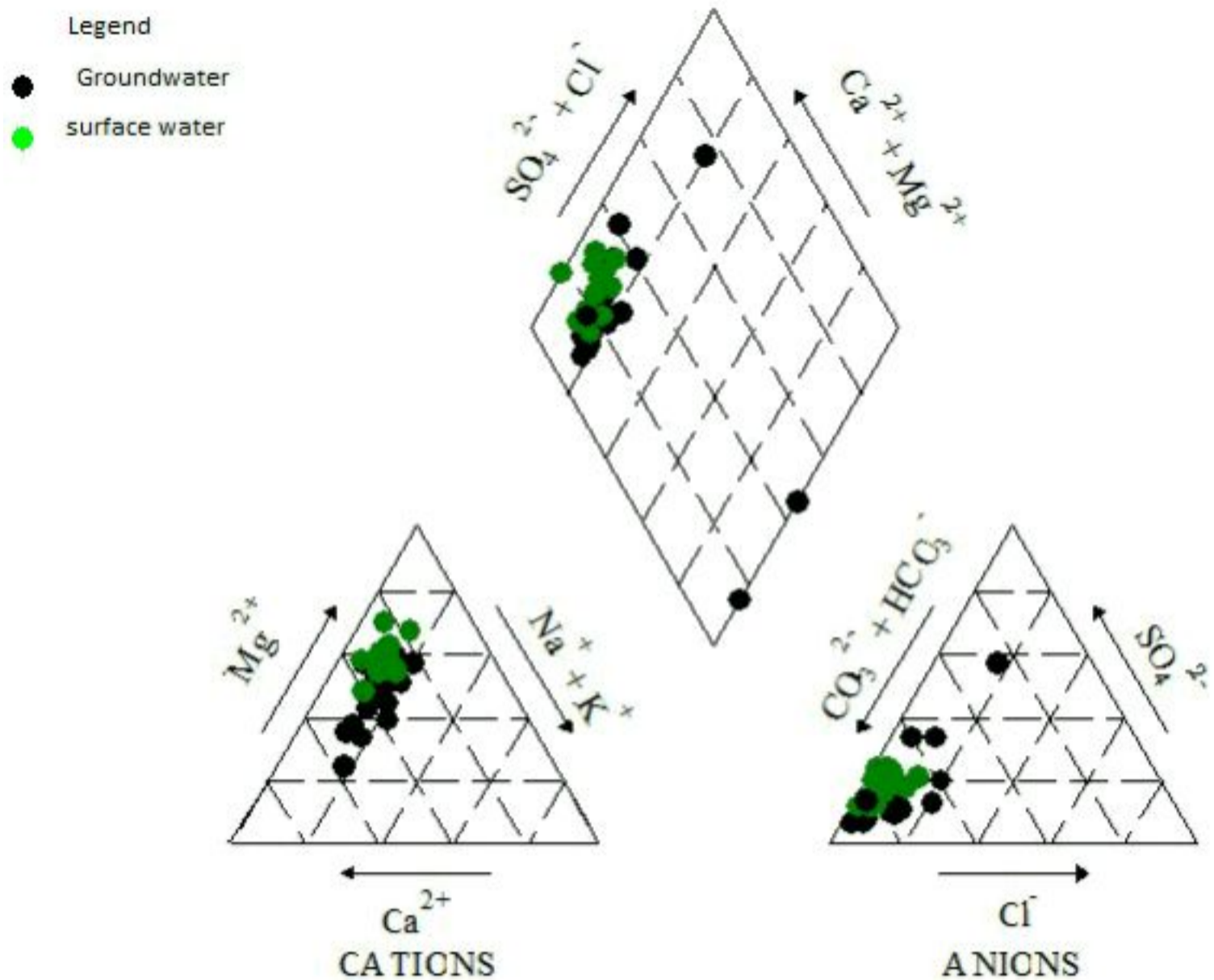


Fig. 4.9: Piper diagram showing the hydrochemical facies of the study area.

From the Piper diagram (Fig. 4.9), about 98% of samples fell on the $\text{Ca}^{2+} + \text{Mg}^{2+}$ and $\text{HCO}_3^- + \text{CO}_3^{2-}$ section of the diamond field making Ca-Mg- HCO_3 the dominant water type for both groundwater and surface water. And about 2% of the sample fell on sodium bicarbonate water type. The mineral composition of rock in a granite terrain is plagioclase, quartz, biotite and hornblende (Ganyaglo et al., 2010). The dissolution of minerals may therefore cause the high concentration of calcium in both waters

whereas magnesium may be produced from hornblende. HCO_3^- can also be generated from atmospheric CO_2 , oxidation of organic and some carbonate rocks. This reaction produces weak carbonic acid that helps the breakdown of mineral in rocks. The evolved water facies may be due to the mineralogical composition of the rock.

The second water type is Na- HCO_3 which is shown by few groundwater samples in the area. The granitoids within the study area may weather to form clay where cation exchange reaction is suspected. Cation-exchange process where calcium plus magnesium ions in water is exchanged with sodium ions in the medium may be responsible for the decrease in Ca^{2+} ions and increase in Na^+ ions. For example Yidana et al. (2010) suggested that the presence of Na- HCO_3 water type in the Voltaian basin is due to ion exchange. Also the dissolution of sodium bearing silicate like sodium feldspar could result in Na- HCO_3 water types. The third water type is mixed Ca-Mg-Cl water type which is shown by about 1% of the groundwater samples in the study area and is insignificant. It is revealed that surface water and groundwater show the same chemical signatures in the Piper diagram, which suggests the possible common source of water chemistry.

4.2.2 Ions Ratios

One of the major factors that affects the chemistry of groundwater is the weathering of rock minerals. According to Kim et al. (2007) a ratio of 1:1 between total cation and alkalinity suggests that mineral weathering is the major process affecting the groundwater chemistry. Feldspar and carbonates are the abundance in the earth's crust and therefore the most important minerals regulating the chemistry of natural waters. Feldspars occupy about 58% of the earth's crust and is more reactive relative to other

silicate minerals. In addition, carbonate minerals such as calcite and dolomite show large influence because their dissolution rates are faster than those of aluminosilicate minerals. The plot between total cation and alkalinity (Fig. 4.10) shown that some of the samples are close to the 1:1 mineral dissolution lines indicating that dissolution of minerals in the groundwater is an important geochemical process governing the chemistry of the groundwater.

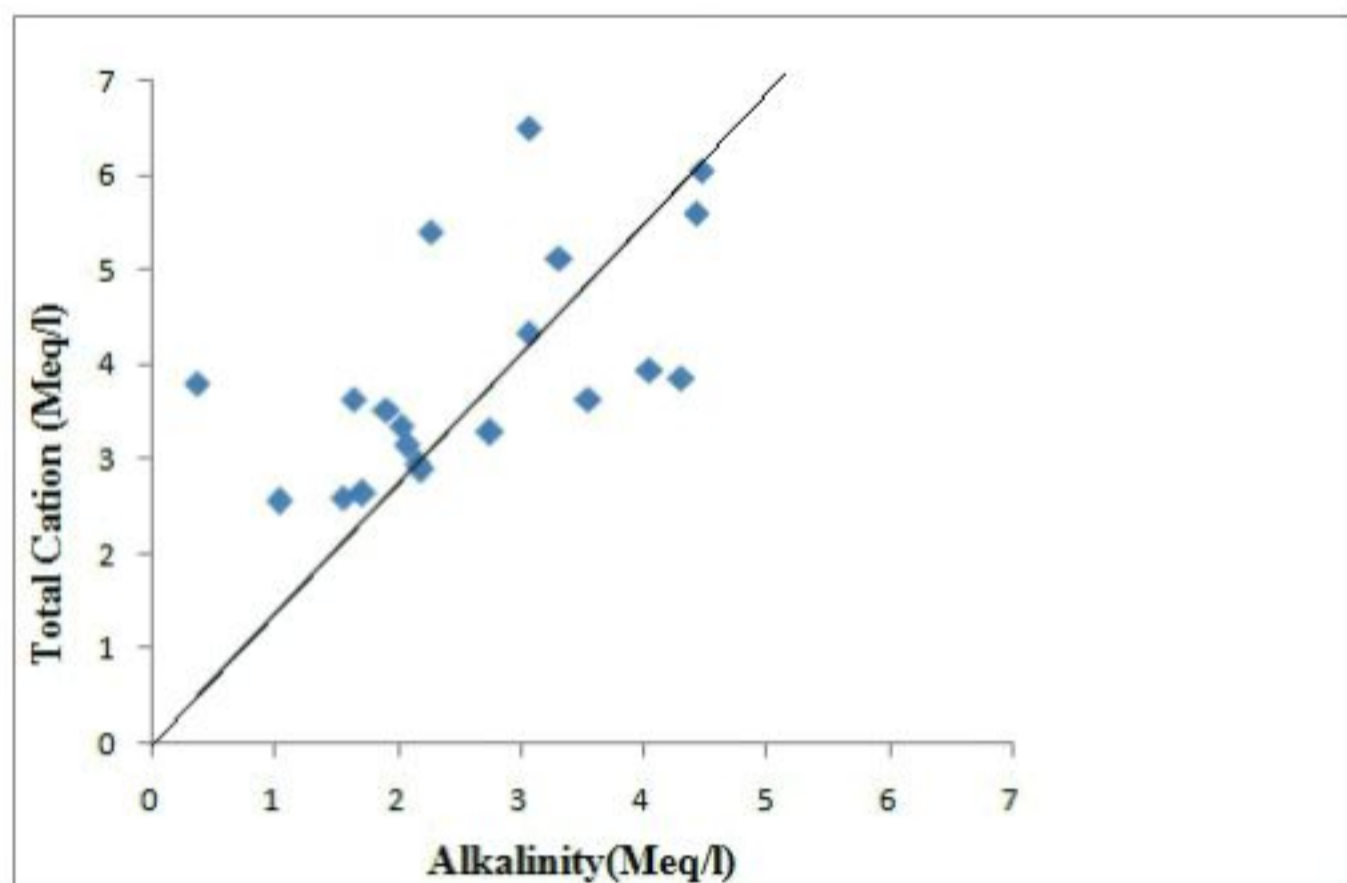


Fig. 4.10: Scatter diagram showing relationship between Alkalinity and total cation.

However, a plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{SO}_4^{2-} + \text{HCO}_3^-$ (Fig. 4.11) provide information on the mineral contribution of calcium, magnesium and bicarbonate in the groundwater of the study area. The plot showed (Fig.4.11) that Ca^{2+} and Mg^{2+} might be originated from sources such as dissolution or ion exchange or both processes. In $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{SO}_4^{2-} + \text{HCO}_3^-$ plot, the point fell along the equiline that is $\text{Ca}^{2+} + \text{Mg}^{2+} = \text{SO}_4^{2-} + \text{HCO}_3^-$ suggested that the ion was from silicate and carbonate weathering (Datta and Tyagi., 1996). Some of the points in the study fell on and

around the equiline that is 1;1 meaning that carbonate weathering was the hydrogeochemical process operating in the region. The plot also shows that majority of the groundwater samples fall below and above the 1:1 line indicating ion exchange as process generating Ca^{2+} and Mg^{2+} ions in the groundwater. Therefore there are three processes that Ca^{2+} and Mg^{2+} can be derived from; silicate, carbonate weathering and ion exchange.

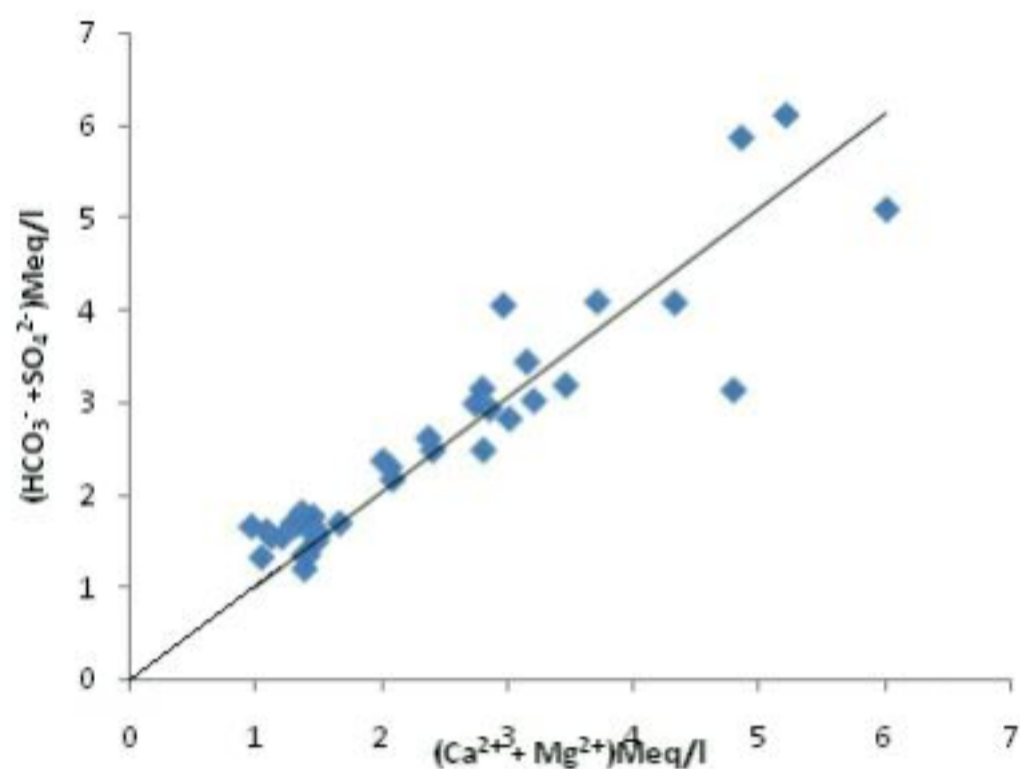


Fig. 4.11: Scatter plot of $\text{Ca}^{2+} + \text{Mg}^{2+}$ verse $\text{SO}_4^{2-} + \text{HCO}_3^-$ showing carbonate and silicate weathering of the study area.

On the other hand, if the dissolution of dolomite (MgCaCO_3) and calcite (CaCO_3) are the main carbonate mineral from which Ca^{2+} and Mg^{2+} enter the ground, these can be shown by the molar ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$. Mayo and Louks (1995) and Katz et. al., 1998 explained that if $\text{Ca}^{2+}/\text{Mg}^{2+} = 1$ or below 1, dissolution of dolomite will occur whereas greater than 1 and equal to 2 was an indication of calcite dissolution and above 2 (i.e excess Ca over Mg) would show silicate dissolution (Katz et al., 1998).

The plot of $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio of groundwater samples in the study area (figure 4.12), revealed that silicate weathering was also a process that had an impact on the water chemistry but very minimal since only a few of the samples fell above a ratio greater than 2. The study area is characterized mainly by granitic rocks that have appreciable amount of silica that may react to produce ions into the water. This silicate minerals are slow to weathering and therefore release less ions into the water. Most of the samples fell in the less than 1 portion indicating contribution from dissolution of carbonate and samples between 1 and 2 portions attributing to dolomite dissolution.

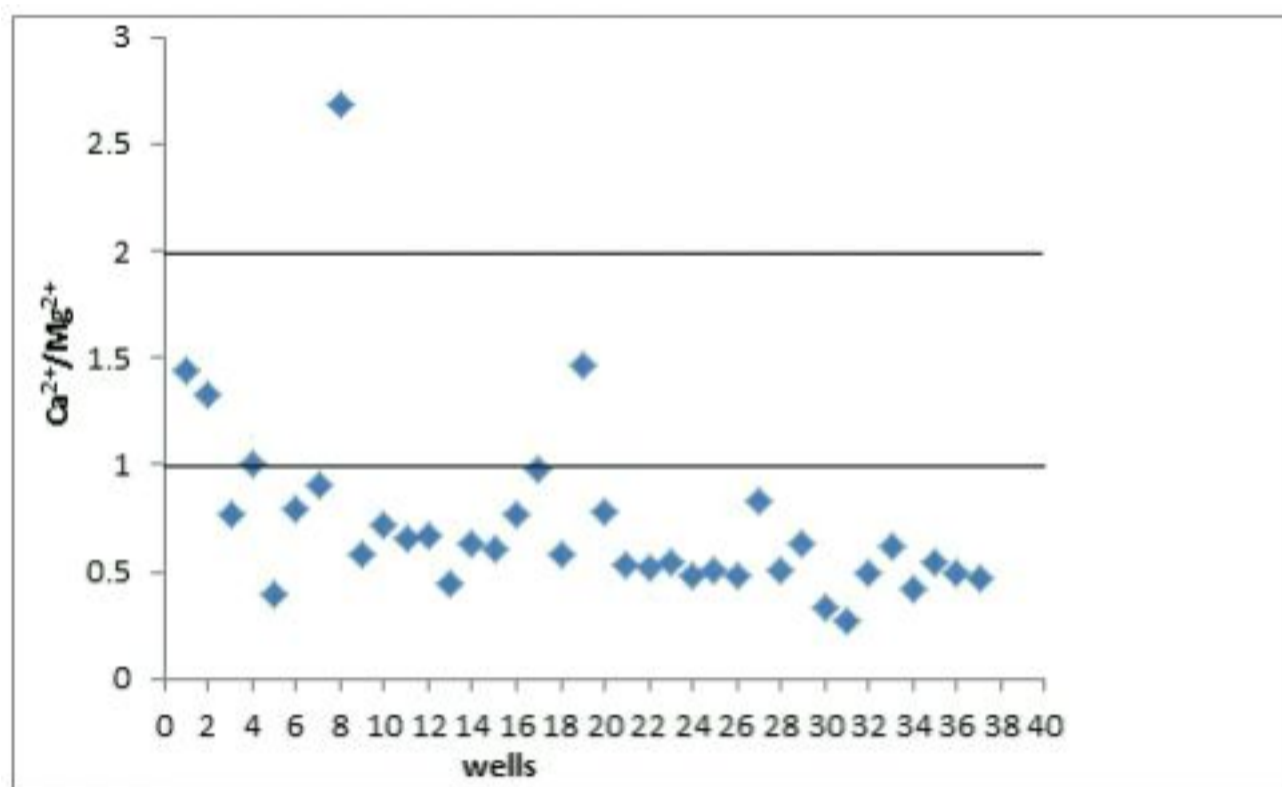


Fig. 4.12: Scatter plot of $\text{Ca}^{2+}/\text{Mg}^{2+}$ ratio of groundwater samples against the wells of the study area.

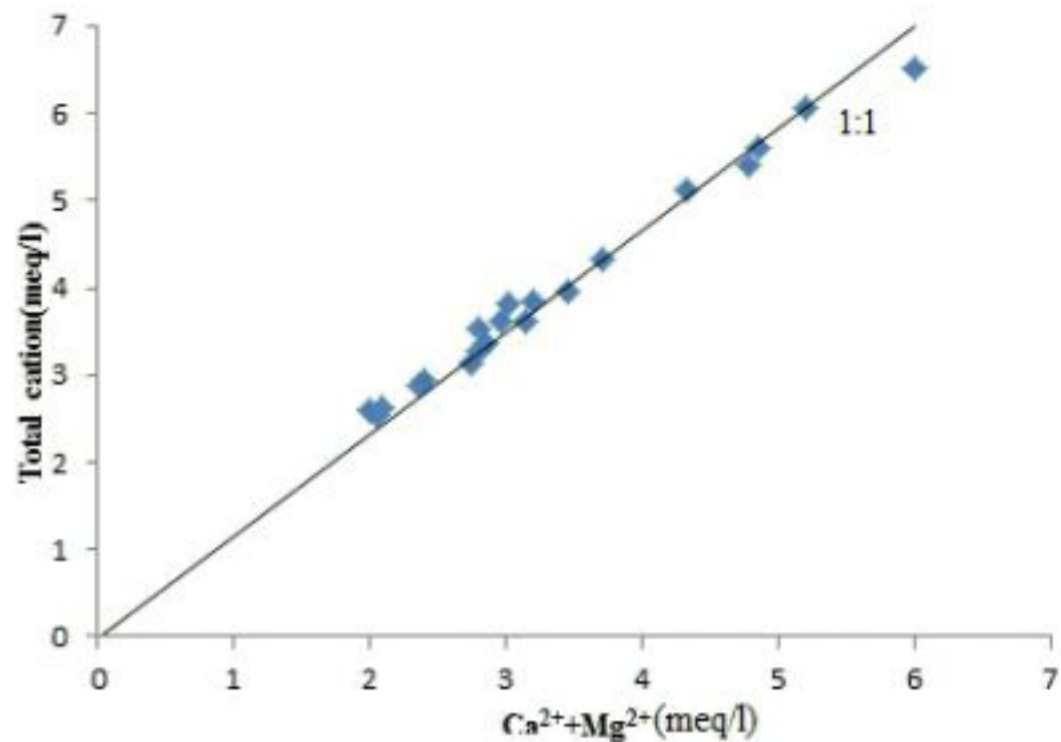


Fig. 4.13: Total cation verse $\text{Ca}^{2+} + \text{Mg}^{2+}$ plot of the study area.

The dissolution of halite in groundwater releases equal concentration of Na^+ and Cl^- into solution (Uma et al., 1990). The plot of Na-Cl (Fig. 4.14) showed that most samples deviated from the expected 1:1 ratio indicating that Na^+ and Cl^- were derived from other process. A Na^+/Cl^- ratio greater than 1 reflects Na^+ released from Na bearing silicate rock reaction (Meybeck, 1987). The ratio of Na^+/Cl^- showed greater than 1 for most of the samples, the excess Na^+ above the 1:1 line was likely to come from Na-bearing silicate rock, perhaps plagioclase and Feldspars dissolution. On the other hand, the ratio of $\text{Na}^+/\text{Cl}^- < 1$ indicating sodium level was low in the groundwater which could be due to ion exchange.

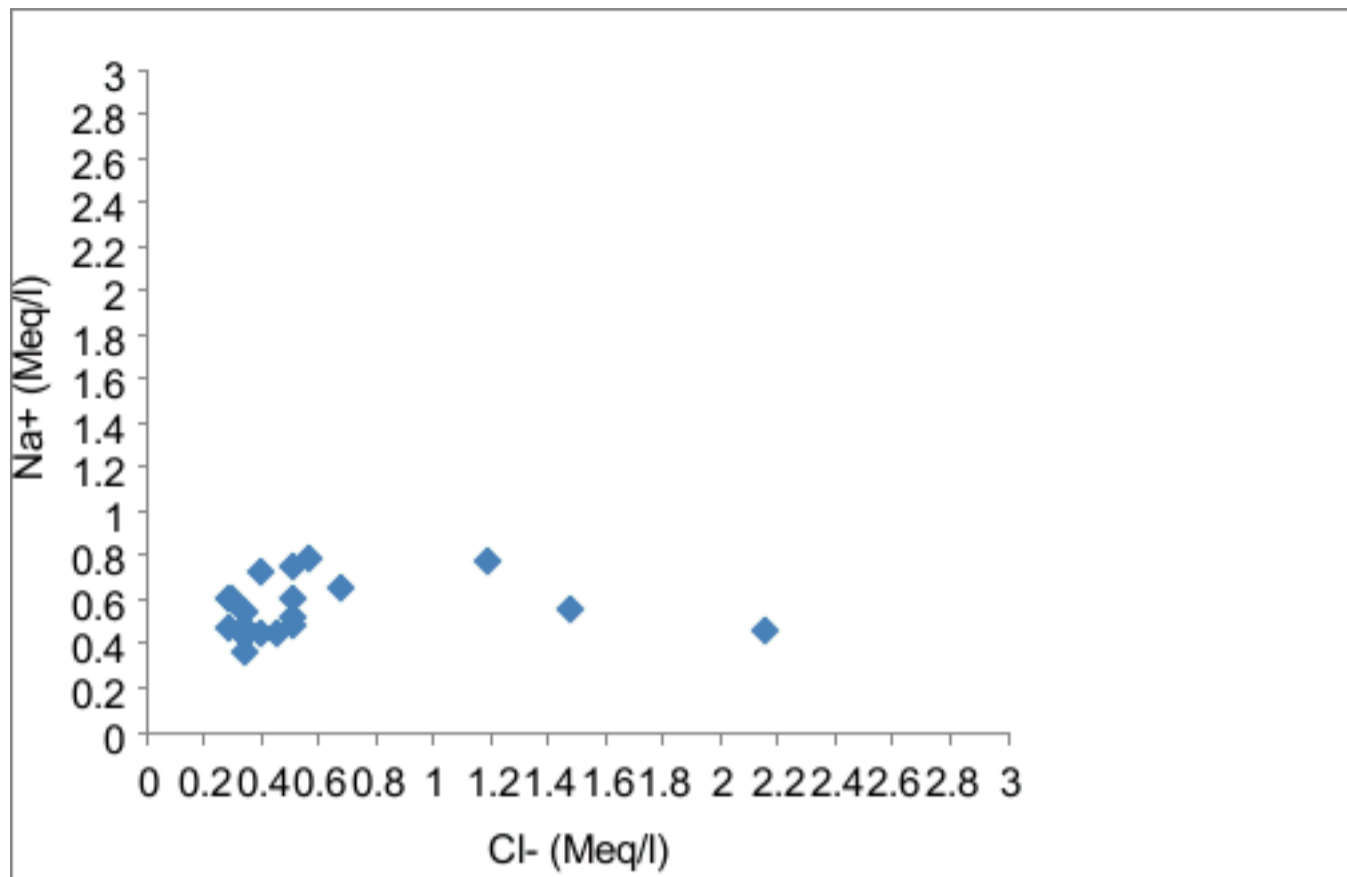


Fig. 4.14: Bivariate plot of Na⁺ against Cl⁻

Ion exchange could also influence hydrochemistry in some parts of the crystalline rocks. Effect of ion exchange in the groundwater chemistry was evaluated by the Chloro alkaline indices (CAI 1 and 2) suggested by Schoeller (1967). CAI 1 and 2 were calculated using the Equation 12 and 13 respectively.

$$CAI1 = \frac{Cl^-}{Cl^- + HCO_3^-} \quad (3.1)$$

$$CAI2 = \frac{Na^+ + K^+}{Na^+ + K^+ + Ca^{2+}} \quad (3.2)$$

In ion exchange process, Ca²⁺ and Mg²⁺ from groundwater will be exchanged with Na⁺ and K⁺ from the aquifer material. In this case, both the indices will yield negative

values and for a reverse exchange process, the indices will be positive (Nagaraju et al. 2006; Ishaku et al., 2011) meaning that Na^+ and K^+ from the water is exchange with Ca^{2+} and Mg^{2+} from the aquifer material.

In the present study, almost all the samples showed a negative value for both indices, suggesting that the normal ion exchange process was more prominent. However, three wells in the study, showed positive values for both indices, thus, reverse ion exchange also contributes but little as compared to ion exchange. A plot of CAI 1 and CAI 2 for this study are as shown in Figures. 4.15 a and 4.15 b. It is obvious that Na^+ in the groundwater is controlled by rock weathering and ion exchange

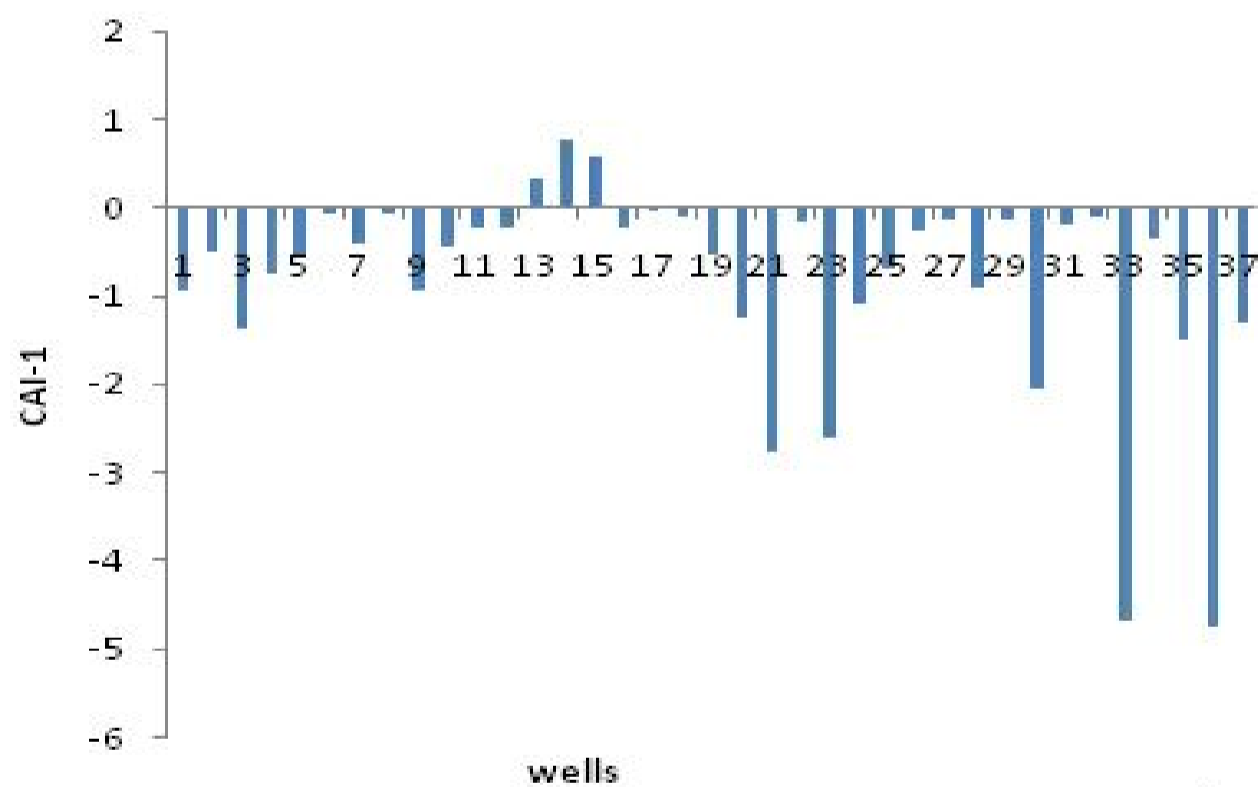


Fig. 4.15 a: A plot of CAI-1 against sample point of the study area.

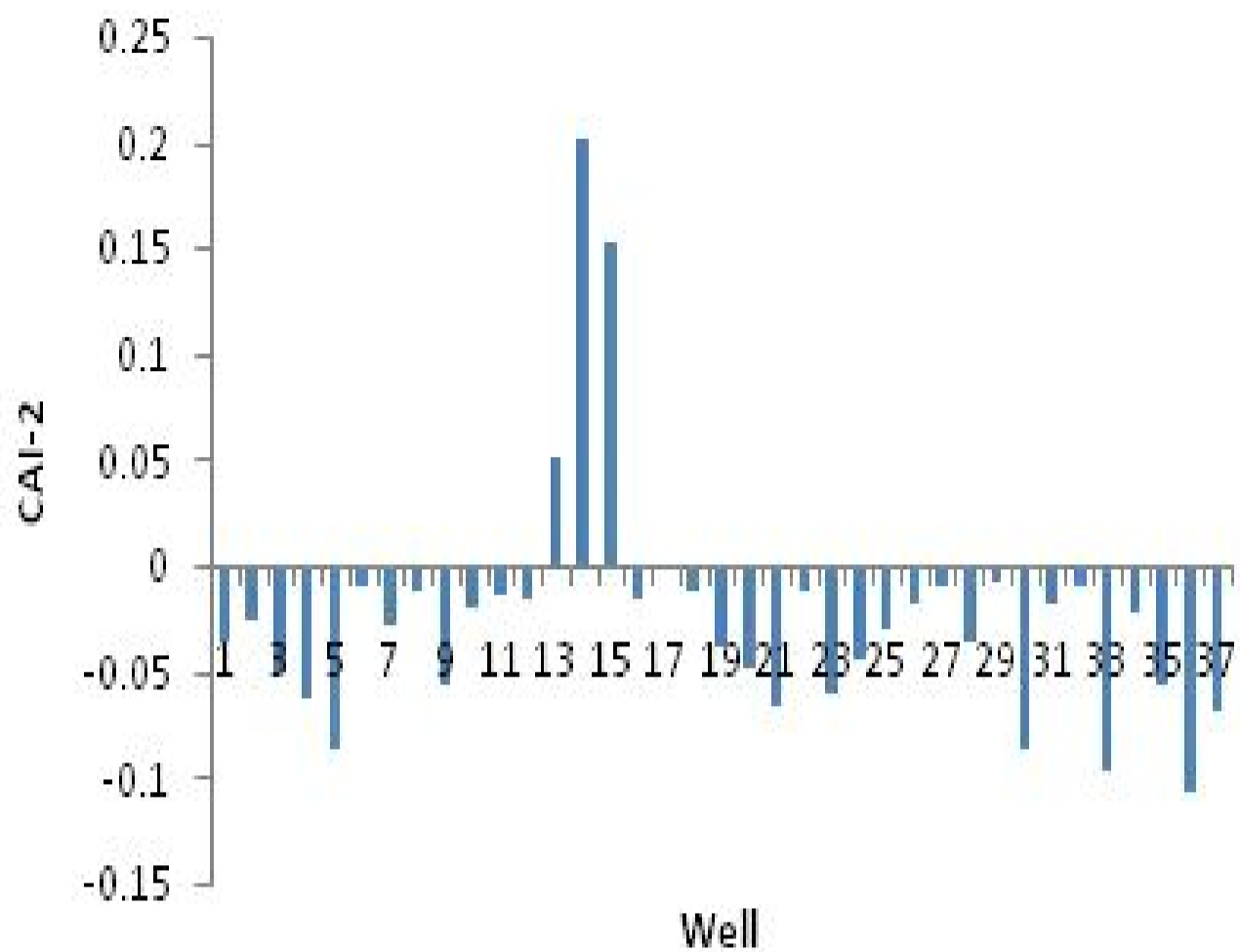


Fig. 4.15 b: A plot of CAI-2 against sample point.

4.2.3 Multivariate statistical methods

Hierarchical cluster analysis applied simultaneously with other graphical methods have been useful in characterizing hydrochemical processes and providing clues to groundwater flow paths. Several writers have used this method to identify causes of variations in the hydrochemistry of groundwater. For instance, Yidana et al. (2012b) used hierarchical cluster analysis to distinguish anthropogenic sources from the natural sources in the variation of hydrochemistry in aquifer underlying the Ankobra Basin. Also results from R-mode HCA of groundwater from the Northern Region of Ghana reflect the influence of both natural and anthropogenic factors on the groundwater chemistry (Loh et al., 2012). Therefore the application of HCA techniques in the interpretation of chemical data provides the hydrogeologist with a powerful problem-solving tool, giving insights to geochemical and anthropogenic

processes affecting groundwater resources and groundwater quality.

R-mode HCA performed on the physico-chemical parameters of the groundwater using Ward's linkage method and Euclidean distance measurement technique generated two main clusters (Fig. 4.16); one formed by EC, Mg^{2+} , HCO_3^- , Ca^{2+} , K^+ , Na^+ and the second cluster is made of Cl^- , NO_3^- and SO_4^{2-} . The first cluster showed strong mutual correlation among EC, Mg^{2+} , Ca^{2+} and HCO_3^- while the Na^+ , and K^+ also shown little correlation. The cluster similarities is based on the multi-dimensional space between parameter and their position on the dendrogram. The cluster showed that the chemistry of the groundwater may probably be coming from rock weathering or leaching of mineral from water rock interaction. It also showed that the high values of EC in the groundwater may be derived from Mg^{2+} and HCO_3^- .

The second cluster is made up of Cl^- , SO_4^{2-} and NO_3^- which mostly is an indication of contamination from anthropogenic activities. This chemistry could be arising from the poor sanitation conditions around the boreholes. Boreholes in the area are constructed with waste water collection pond so close to them. Again, the application of fertilizers and animal droppings as manure on the nearby farmlands may be the main contribution factor of ammonia which react to form nitrate in the groundwater.

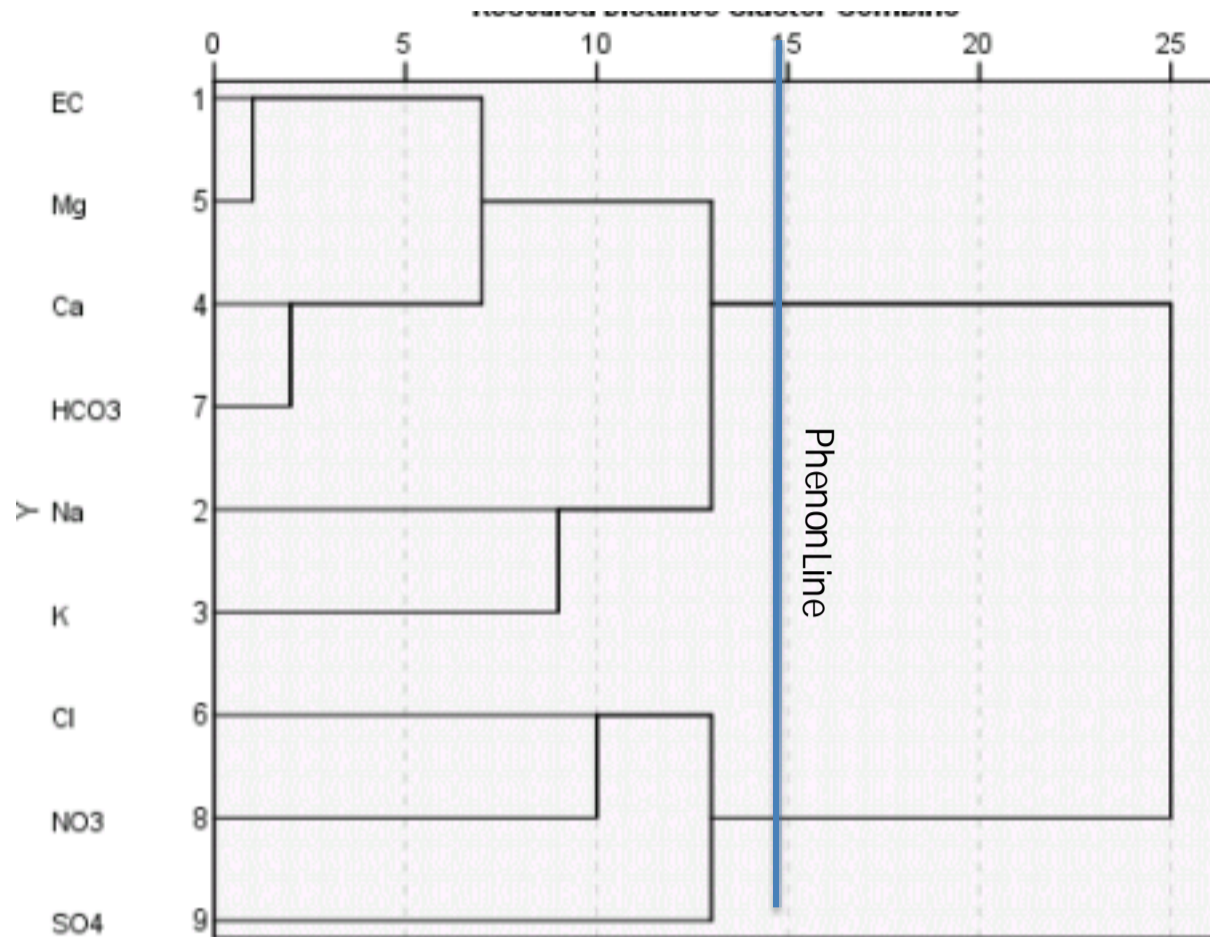


Fig. 4.16: Dendrogram showing the various cluster of element in the study area.

Principal component (PC) analysis is a scientific method performed to reduce a large number of variables into component which bring out strong pattern in a dataset for easier interperatation. This number of component extracted determines the number of possible different sources of variations in the data set. In groundwater chemistry, components are extracted based on the physical and chemical processes such as dissolution, ion exchange and anthropogenic activities that are taking place within the aquifer. The components extracted, are ranked in order of merit. The PC with the highest eigen values greater than one is placed first and it determines the most important sources of variation in the data set and the next component usually indicates the progressively less important processes contributing to the chemical variation. This method has been successfully applied to clarify natural and anthropogenic process affecting groundwater quality in the coastal plain (Gular et al., 2012).

The principal component analysis (Table 4.6) using Kaiser Criterion and varimax rotation resulted in three main components which accounted for over 73% of the total variance in the hydrochemistry. The third PC did not have high loading for any of parameter greater than 0.5 except Na^+ which has just 0.5. It implies that the third PC will not contribute any significant source of variation to the hydrochemistry and was therefore dropped.

The results show that the first and second PCs account for more than 62.14% of the total variance (Table 4.7), which is quite good and can be relied upon to identify the main sources of variation in the hydrochemistry. Component 1 represented about 38% of the total variance in the hydrochemistry and has high absolute loading (greater than 0.5) for HCO_3^- , pH, EC, Mg^{2+} , K^+ , Ca^{2+} , and Na^+ . The positive loading for Mg^{2+} , Ca^{2+} , Na^+ , and HCO_3^- (Table 4.9) may result from rock water reactions such as dissolution of clay minerals and other silicate mineral. Granite is the main rock type in the area and the dissolution of these rocks will release these ions into the water. The positive factor loading for EC also implies that it was controlled by the contribution of Mg^{2+} , HCO_3^- , Na^+ , and SO_4^{2-} . Component 2 which accounted for 24.17% of the total variance, contained high loadings for SO_4^{2-} , NO_3^- and Cl^- which was an indication of contamination from anthropogenic processes. The PC scores for various parameters in the data sets were plotted in a 2D scatter-plot that is PC1 vs PC2. The spatial distribution of variable of PC scores for the datasets suggests a continuous variation of the chemical and physical properties of some of the samples. In Fig. 4.17, the variable with high loading for PC 1 and 2 were well separated in the 2D scatter plot.

Table 4.6: Varimax rotation PCA loading matrix

	PC1	PC2	PC3
EC	.889	.392	-.082
HCO ₃ ⁻	.813	-.458	-.301
Ca ²⁺	.790	.003	-.054
Na ⁺	.639	-.264	.561
PH	.594	-.560	-.126
Mg ²⁺	.550	.432	-.516
K ⁺	.505	-.406	.420
NO ₃ ⁻	-.075	.809	.208
Cl ⁻	.483	.585	-.017
SO ₄ ²⁻	.474	.568	.365

Table 4.7: Percentage variance explained by each of the factors in the factor model.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.857	38.566	38.566	3.857	38.566	38.566	3.095	30.950	30.950
2	2.417	24.172	62.738	2.417	24.172	62.738	2.353	23.527	54.478
3	1.051	10.510	73.248	1.051	10.510	73.248	1.877	18.770	73.248
4	.948	9.483	82.731						
5	.774	7.744	90.475						
6	.381	3.805	94.280						
7	.297	2.967	97.248						
8	.226	2.256	99.504						
9	.030	.299	99.803						
10	.020	.197	100.000						

The close distribution of the variable of PC1 and PC2 on the scatter diagram suggested that all the parameters had similar flow paths or sources. If distribution of the variables on the diagram was broad it would indicate diverse processes in acquiring the chemical property. The results of the plot showed that variables are well separated in the PC space differentiating the natural process through which PC1 variable acquired its chemical characteristic from the anthropogenic sources through which PC2 variables acquired its character.

During rock-water minerals present in different type of rocks will completely or partially dissolve to release ions into water based on the resistance of the rock to chemical weathering. Therefore ratios between ions are useful in establishing the sources of major constituent of groundwater and their evolutionary pattern. The type of mineral responsible and their chemical similarity could also be identified by ions ratios.

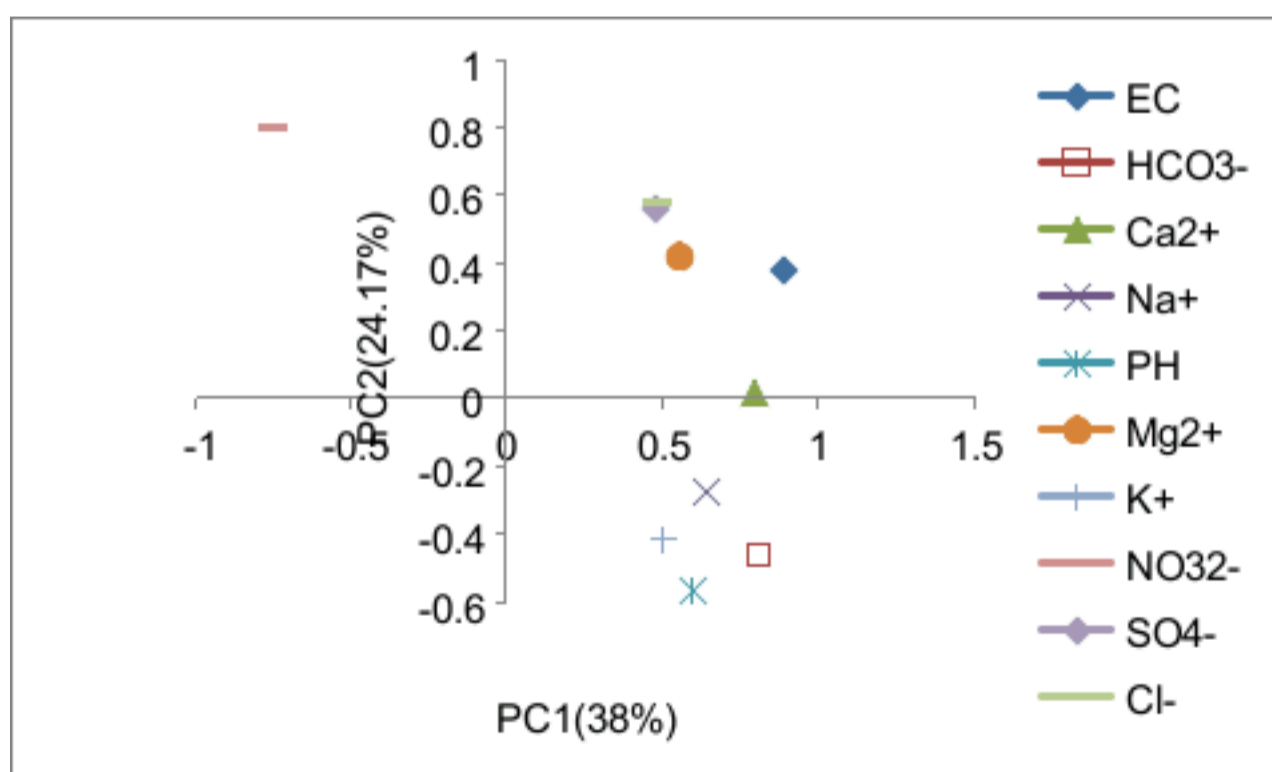


Fig. 4.17: Spatial distributions of the variables in PC 1 and PC 2

4.3 ISOTOPE ANALYSIS OF WATER

Many writers have used oxygen and hydrogen isotopes of water as tracers to understand hydrogeological processes such as precipitation, groundwater recharge and surface water interactions. A comparison of the oxygen and hydrogen isotopic compositions of precipitation, groundwater and surface water provide a good method for evaluating the recharge mechanism.

Groundwater stable isotopic variation is largely determined by recharge conditions and processes in the soil zone. In groundwater, geochemical behaviour with different oxygen and hydrogen bearing mineral or compounds in the subsurface during very long residence time at high temperature can modify their concentration.

The range of values of ^{18}O in groundwater from the study area was -3.87% to -2.21 %, and ^2H is -20.9% to -4.43 %. The mean values of ^{18}O and ^2H were -3.18% and -18.35 %, respectively. The ^{18}O and ^2H isotopic concentrations of surface water ranged from -1.20% to -0.57% with a mean of -0.82% and from -6.5% to -1.8% with a mean of -3.97%, respectively.

In the process of evaporation and condensation a sequence of isotope fractionations occur causing variations in the composition of the isotope values of oxygen and hydrogen in meteoric water. Since this fractionation process is based on the equilibrium processes of the isotopes of evaporation and condensation, there is a specific relationship that governs the distributions of isotope values of oxygen and

hydrogen in rainfall. The empirical equation was found by Craig when he used a linear regression method to analyze the composition of the isotopes of oxygen and hydrogen in samples of precipitation, snow water, and river water from all over the world. His finding is known as the Global Meteoric Water Line (GMWL): after the equation of Craig (1961)

$$^2\text{H} = 8.13 \ ^{18}\text{O} + 10.30 \quad 4.1$$

This GMWL is a good reference line for understanding and tracing the origin and movement of water within the environment. However, some specific areas that have different evaporation and condensation conditions create their own special local meteoric water line with a different slope and intercept.

In the plot of ^2H against ^{18}O of the analysed samples (Fig 4.20) two meteoric water lines were inserted. These included Global meteoric water line (GMWL) by Craig (1961) and that of local meteoric water line (LMWL) by Akiti (1980).

$$^2\text{H} = 7.86 \ ^{18}\text{O} + 13.6 \quad 4.2$$

The slope of the GMWL is related to the evaporation or condensation fractionation factor of the ratio of ^2H and ^{18}O of the water (Clark and Fritz, 1997; Faure, 1998) and according to Dansgaard (1964), the intercept of GMWL represents the deuterium excess (d excess).

Akiti (1980) stated that both slope and intercept (d-excess) may vary depending on the

prevailing local climatic and geographic conditions. The slope and intercept of the LMWL (Equation. 4.2) for the Upper East Region of Ghana indicated precipitation that occurred in a warmer/dryer climate where significant amount of rainfall evaporate before reaching the ground. Consequently, low slope and intercept (d-excess) were obtained and compared to that of the GMWL.

The plot of ^{18}O against ^2H (Fig. 4.18) showed that majority of the groundwater samples clustered around the global meteoric water line indicating there eas predominant rainfall sources of recharge without significant evaporation. However a few plotted below the line meaning that the isotopic signature of groundwater may be partially evaporated during rainfall infiltration or as it under went mixing with older water in the aquifer as a similar event was stated by Barnes and Turner (1998) or probably a gaseous exchange (IAEA, 1983).

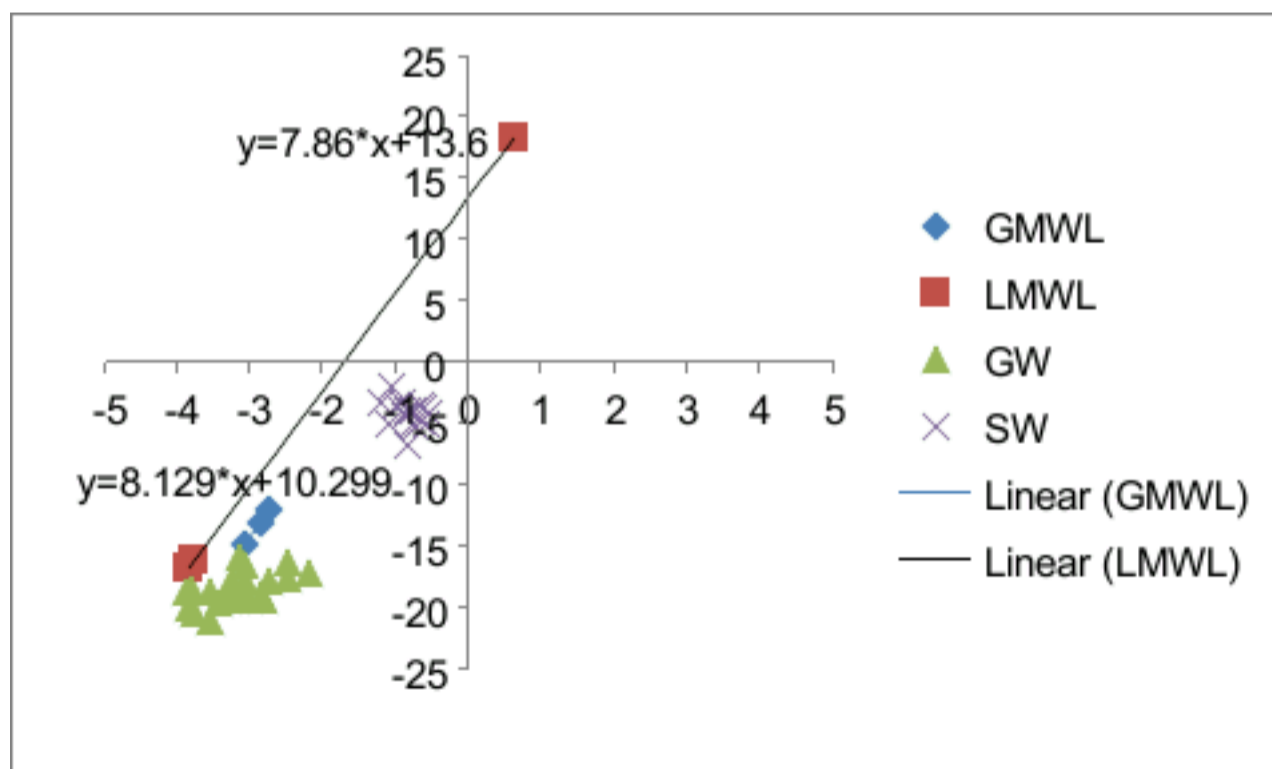


Fig. 4.18: plot of ^{18}O against ^2H of the study area

Surface water data deviated from the Local meteoric water line and plotted sub-parallel (upper right corner) to both meteoric water line indicating some degree of evaporation and relatively enrichment in ^2H and ^{18}O as a similar event was stated by Coplen et al., (2000). The catchment area is hot and semi-arid with large open area therefore experience high evaporation which affect the stable isotopes. Clark and Fritz (1997) noted that displacements from GMWLs usually result in evaporation line with low slope of 8.13 hence the evaporation effect alone in the dam is shown by the low slope value of the surface water evaporation line ^2H - ^{18}O as compare with the local meteoric water line.

$$^2\text{H}=4.003 \ ^{18}\text{O}$$

4.3

The relationship between surface water and groundwater within the study area is an important aspect of characterizing the hydrological system. The variations in the isotopic compositions of the groundwater from that of surface water may be an indication of some modification that existed in the circulation process, groundwater types and sources of recharge (Clark and Fritz, 1997). Furthermore, the isotopic composition of both water are plotted parallel in line which define a single trend. This suggests similar initial precipitation sources of recharge, but under different environmental condition.

The plot of SWL and GWL did not show any intersection with the ranges of isotopes data of both of the groundwater and surface water bodies. This Indicated that groundwater does not contribute to surface water nor the opposite hence no hydraulic connection between both water resources.

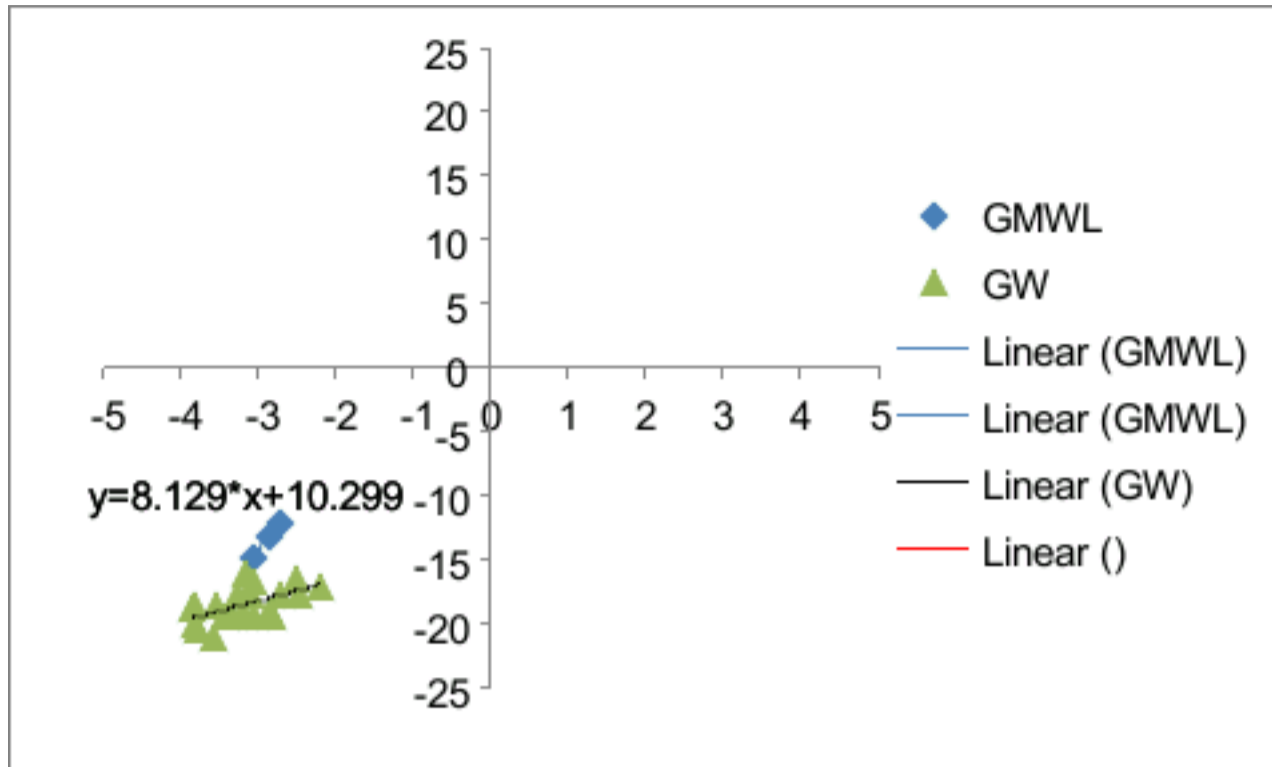


Fig. 4.19: Relationship between isotope of groundwater and surface water of the study area.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Hydrochemical and isotopic studies of groundwater and surface water were carried out around Veia area in Bongo district, Ghana. The processes that controlled the groundwater and surface water chemistry as well as the suitability of the waters for drinking and irrigation purposes were assessed. The relationship between the surface and groundwater and sources of recharge were also established.

This study revealed that the groundwater in the study was is fresh, slightly acidic to neutral, and hard to very hard. The order of abundance of major ions in the groundwater was as found to be: $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$ and $\text{HCO}_3 > \text{SO}_4 > \text{Cl}$ water. The physico-chemical parameters were within the WHO guidelines limit for drinking water with the exception of fluoride which was above the WHO guideline values in most of the samples. Dissolution of fluorite (CaF_2) in the granitoid is the possible source of the high fluoride.

An evaluation of the suitability of both groundwater and surface water for irrigation purposes based on salinity, sodicity, residual sodium carbonate (RSC), permeability index and magnesium hazards (MH) revealed that the water in the area was generally suitable for irrigation.

Irrigation water classification based on SAR values indicated that almost all samples belong to the excellent category. The analytical data plotted on the US salinity

diagram illustrated that two irrigation water types were identified, C1S1, indicating low salinity and low sodium water and C2S1 indicating medium salinity and low sodium water. The Wilcox diagram also showed excellent to good category for irrigation. Based on the classification of irrigation water according to the RSC values, all of groundwater samples belonged to the good category.

Characterization of water using Piper diagram indicated Ca-Mg-HCO₃, Ca-Mg-Cl and Na-HCO₃ as the principal water types with Ca-Mg-HCO₃ being the major water type (about 97%). R-mode HCA performed on the samples revealed three main clusters based on the spatial variations in their hydrochemistry.

The results of the compositional relationship between major ions indicated minerals weathering processes involving carbonate minerals, silicate mineral weathering and ion exchange as the factors controlling the hydrochemistry of groundwater resources.

The results of stable isotope data analysis of groundwater and surface water indicate that both water bodies receive recharge by direct infiltration of evaporated recent meteoric water. The surface water was enriched as compared to groundwater and also clusters exclusively from the groundwater samples point suggesting no hydraulic connection between the two reservoirs.

5.2 RECOMMENDATION

Groundwater is a major source of water supply in Bongo District. Improved management of groundwater resources is a key for meeting future water demands (Anthony Rendon and Richard Bloom, 2014). In order to develop and manage groundwater resources sustainably for long-term water supply, some recommendations are proposed as following:

- Groundwater development projects should be coupled with fluoride treatment.
- Frequent monitoring of groundwater and surface water quality are needed for early detection of potential source of contamination in order to protect the groundwater resource.
- Effective management requires awareness of the status of groundwater quantity available. Therefore further research should be conducted in order to know the volume of water that can be abstracted and readily available for irrigation and its sustainability.
- The people should also be educated on how to improve sanitation by constructing proper soak away pits a few distance away from the water points to avoid contamination of groundwater

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