UNIVERSITY OF GHANA

HYDROGEOCHEMICAL STUDIES OF GROUNDWATER IN THE SOUTHWESTERN COASTAL DISTRICTS OF THE CENTRAL REGION, GHANA.

BY

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DECLARATION

I do declare that, except for the references to other people's work which have been cited, this work submitted as a dissertation work to the Department of Earth Science, University of Ghana, Legon, Ghana for a degree of Master of Science in Groundwater Resource Development is the result of my own research and has not been presented for any degree.

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ABSTRACT

The hydrogeochemical data of groundwater of southwestern coastal Districts of the Central Region of Ghana were examined to determine the main factors controlling the groundwater chemistry and study the resultant water type formed in order to determine the suitability of the water for different uses. Different geochemical interpretation methods were used to identify the geochemical characteristics.

The pH values of groundwater samples showed that 36 samples had pH values below lower limit of 6.5 WHO (2011). Based on TH, groundwater quality ranges from soft to very hard. The hardness in the study was adduced to be from sedimentary rocks seepage and runoff which may be aggravated by detergents and soaps. The groundwater in the study area falls under fresh (TDS<1000 mg/l) to brackish (TDS>1000 mg/L) types of water.

The Ca^{2+}+Mg^{2+} vs. HCO_3^-+SO_4^{2-} scatter diagram showed that majority of the samples fall above the equiline indicating that silicate weathering is the dominant process for supply of the magnesium and calcium ions to the groundwater. The concentration of Na^+ and K^+ in the ground water is a made possible by halite dissolution process (Na^+/Cl^- is approximately 1). Also, the relationship between Na+K-Cl and Ca+Mg-HCO_3+SO_4 showed that there is ion exchange of Na^+ and K^+ in water for Ca^{2+} and Mg^{2+} from rock (aquifer) (Bhat et al., 2013).

Concentration of HCO_3^- in the study area shows that approximately 9.4% (6 samples) of the sampling stations have values exceeding the allowable limit of 240 mg/L set by the WHO (2011) guidelines for drinking water (Table 4.6).

The values of manganese found was between 0 and 3.3 mg/L with as many as 39 samples representing about 60.9% found to be above the WHO (2011) allowable limit of 0.1 mg/L in potable water.

The values obtained from the physicochemical analysis of groundwater samples indicated that the dominant cation in the area is Na^+ and the anion is Cl^-, and the order of dominance ions is $Na^+ > Ca^{2+} > Mg^{2+} > K^+ : Cl^- > HCO_3^- > SO_4^{2-}$. Piper Diagram showes the general dominant water type as NaCl.

Sodium measured against Ca^{2+} and Mg^{2+} falled outside the permissible limit of 1.0 meq/L and are considered unsuitable for irrigation purposes. The TDS values are with values less than 1000 mg/L and are within the nonsaline category, and are therefore classified as excellent irrigation waters (Robinove et al., 1958).

DEDICATION

I dedicate this work to my parents, my beloved wife Mrs. Patience Dzifa Ayimah and my son Selase Korsi Ayimah.

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CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND TO STUDY

The most important natural resource which is vital for all life on earth is water (Reddy, 201l) on which, the well-being and development of society is dependent upon. Water is also identified as one of the most important natural resources because it is viewed as a key to prosperity and wealth (Arbues et al., 2003). Even though water is the most precious resource, it is sometimes scarce or abundant and is always very unevenly distributed both in space and time (Reddy, 2011).

World Commission for Water (2000), estimates that more than 1 billion people in developing countries do not have access to clean water whilst 2 billion lack adequate sanitation. According to Ruddy (2011), Europe and Asia in all have only 27% of World's fresh water though they accommodate about 76% of world's population.

Over-exploitation of groundwater along coastal area is an environmental issue which leads to intrusion of seawater into the inland aquifer (Subba et al., 2005). Subba et al. 2005, also noted that brackish nature in most groundwater in the coastal area is not due to seawater influence, but caused by the hydrogeochemical process and urban waste being the combined source of contamination in a few well at topographic low close to the coast.

Globally, there is an increasing dependence on groundwater for domestic, industrial and agricultural purposes. According to Singh (2009), groundwater is a critical resource for drinking and irrigation in Deoria District of Ganga Plain, India. However, during the last two to three decades, aquifers in the District have deteriorated to a high degree both in quality and quantity due to high population growth and environmental pollution.

Water quality is related to the intended use and therefore any addition of materials to the water beyond the admissible level may render the water unsuitable for one use or the other. For example effluents from mining operations, by virtue of the chemical contained in them, will negatively affect the quality of water sources in neighboring communities as the effluent affect the quality and make them unsuitable for human consumption.

Water quality can be compromised by geogenic and anthropogenic processes. Thus, chemical composition of groundwater depends not only on natural factors such as the lithology of the aquifer, the quality of recharge waters and the type of interaction between water and aquifer, but also on human activities, which can alter these fragile groundwater systems either by polluting them or by changing the hydrological cycle (Lalitha et al., 2010).

Pulido-Bosch et al., (1998), discovered the combined action of the washing out of Miocene marls, dissolution of carbonate rocks, agricultural pollution and seawater intrusion as the probable causes linked to increased salinity at some points of the Temara Aquifer in the coastal zone of northwestern Morocco.

1.2 Problem Statement

There has been a rapid increase in nonpoint sources of groundwater pollution in recent decades, (Lalilha et al., 2004). There are many different sources and processes that can be responsible for the commonly found contaminants and pollutants in groundwater (Lalilha et al., 2004).

Subba et al. (2005) reported that over-exploitation of groundwater results in decline of water levels along the coastal region that was said to be a natural phenomenon. Therefore groundwater quality survey has to be carried out to assess such a phenomenon along the coast of Ghana specifically in the costal districts in Central Region

1.3 Study Objectives

The overall aim of this work is to identify and characterize the hydrogeochemical processes prevailing in the study area and the resultant water types formed, in order to determine the suitability of the water for different uses. Emphasis will be placed on the phenomena that have the potential to compromise the natural chemistry of water.

The specific objectives of this study however are:

- Determine the mechanism controlling hydrochemistry of the groundwater in the study are a.

- Determine the major water types in the study area.
- Evaluate the chemical and physical characteristics of groundwater.
- Determine the suitability of the groundwater in the study area for various uses.

1.4 Justification of the Study

Water Resources Commission has estimated that the consumptive water demand for 2020 is projected to be 5.13m^3 (WRC, 2010) and much of this water demands are being met especially in the rural areas through the construction of boreholes by the state agency such as Community Water and Sanitation (CWSA), and NGO's such as Water aid, World Vision Ghana Rural Water Project (GRWP).

The chemistry composition of the water would determine its suitability for domestic and agricultural uses. This is because; the quality of water affects health and agricultural development of every society. Therefore the study seeks to contribute to understanding the hydrogeochemistry of the water so as to advise its implication for human consumption and for agricultural purposes. It would also establish the hydrogeochemical processes that affect water quality in the study area.

1.5 Study Area

1.5.1 Location and Accesibility

The study area covers three districts of the Central Region in Ghana: namely; Cape Coast Municipality, the Mfantseman Municipality and the Abura Asebu Kwamankese District.

It is bounded to the south by the Gulf of Guinea, to the west by the Komenda Edina Eguafo Abrem Municipal Assembly, to the north by the Twifu Hemang Lower Denkyira District and the east by Gomoa District (Ghana Districts, 2006).

It covers a total area of 980-Km^2 with Cape Coast Municipality, Mfantseman Municipality and Abura Asebu Kwamankese District having Cape Coast, Saltpond and Abura Dunkwa as its capital cities respectively, (Ghana Districts, 2006). Figure 1.0 shows the location map of the study area.

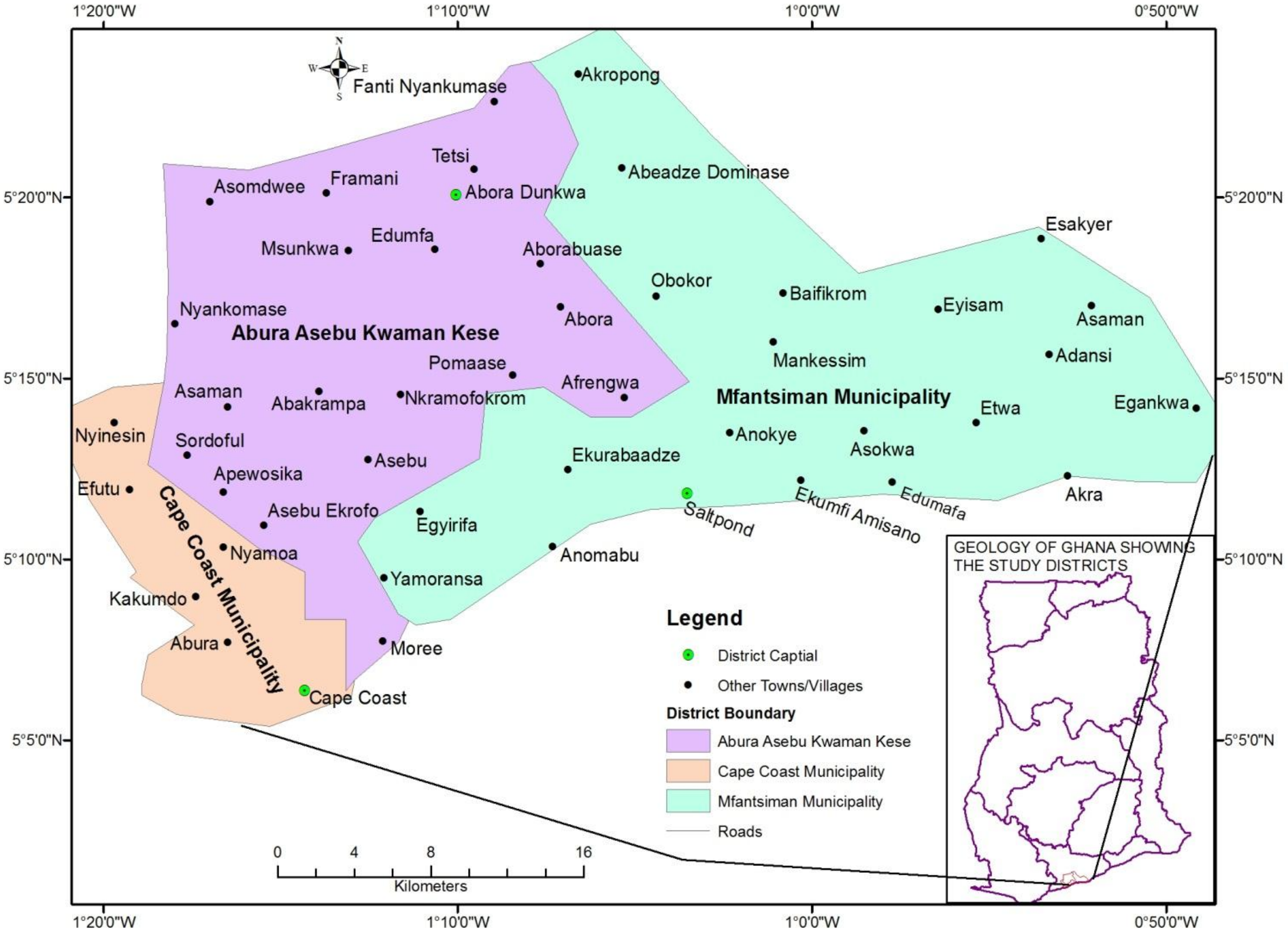

Figure 1.1 Location Map of the study area

1.5.2 Physiography and Vegetation

The study area is dominated by batholiths interspersed with valleys. Located in the valleys are several streams, the largest of which is the Kakum. Many of the steams end in wetlands and the Fosu Lagoon at Bakaano (Ghana Districts, 2006). The wetlands serve as barriers to physical development. In the northern parts of the Abura Asebu Kwamankese district, however, the landscape is generally low lying and is suitable for the cultivation of various crops.

The present vegetation of the study area consists of shrubs, grass and pockets of relatively dense forest found around fetish groves and isolated areas (Ghana Districts, 2006). The vegetation in the southern part of the study area is mainly thin scrub to dense scrub stretching to Asebu area. Kakum National Park (a tropical rainforest) stretches to the northwestern part of the district. The rest of the district is made up of the secondary thick bushes with isolated 'Onyaa' trees and other small sized diameter trees (Mfantseman Dictrict, 2011).

The original vegetation of dense shrubs, which the rainfall supported, has been replaced by secondary vegetation as a result of clearing for farming, charcoal burning, bushfires and other human activities. Presently, trees are less dense in the area compared with the interior forest areas, except the occasional acacia plantations and bamboo shrubs found in a few sanctuaries not yet completely deforested. The northern parts of the municipality are an exception to what has been described. Secondary forests can be found and have survived mainly due to tower population densities and relatively little disturbance of the ecosystem (Ghana Districts, 2006).

1.5.3 Geology and Hydrogeology of the Study Area

The study area also falls within the Birimian basin and the Kibi belt and is underlined mainly underlain by the Precambrian Birimian intruded by Cape Coast-type, granitoid and pegmatites (Yidana, 2010) and the groundwater occurs within the fractures of theses rocks. These rocks are crisscrossed by mafic dykes (dolerite) which was inferred from acromagnetic data (Fig 2.1). Also occurring in the study area, especially the Mfantsiman districts are tertiary rocks very close to the coast, birimian sediments and biotite granitite whiles Cape Coast municipality has the Basin-type Granitoids and the sekondian group of rocks (Devonian) and also in the Abura Asebu Kwaman Kese District has mainly the Basin-type Granitoids and Berimian sediments. The hills are generally overlain by sandy and clayey silts while the valleys are overlain by clayey gravel with lateritic soils exposed in a number of areas (Yidana, 2010).

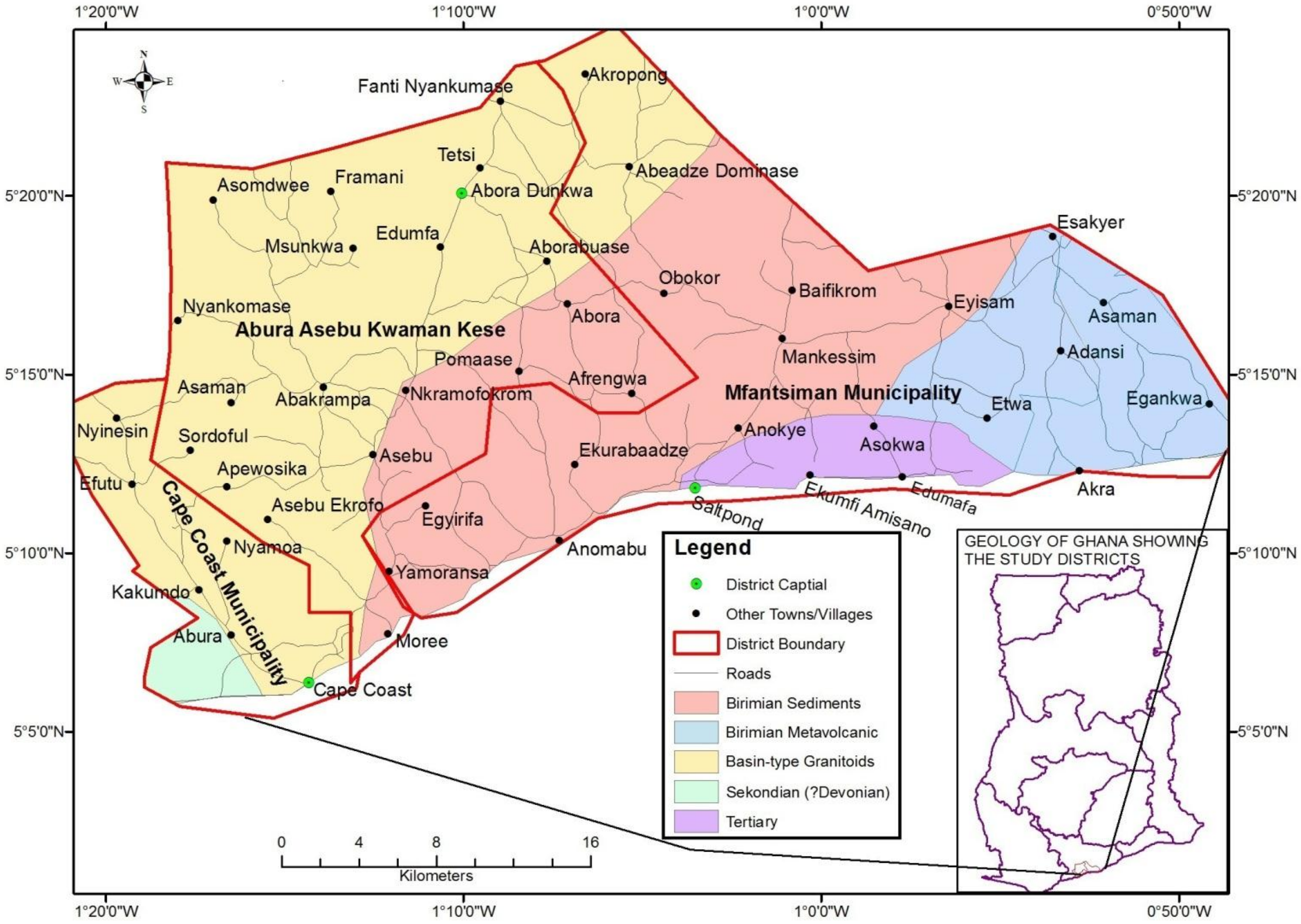

Figure 1.2 Geology of the study area

CHAPTER TWO

LITERATURE REVIEW

2.1. Geology and Hydrogeology of Ghana

The geology of Ghana is dominated by rocks of the Birimian Supergroup of the Early Proterozoic age and post intrusive granitoids, the Tarkwaian System and the unconsolidated sedimentary rocks, with down warping filled Voltaian rocks on the eastern part of the country and the Dahomeyides on the southeastern part of the country. Gill (1969) delineated the hydrogeological Provinces of Ghana from the existing geological map of Ghana and Dapaah-Siakwan and Gyau-Boakye (1998) identified four hydrogeological regions from the overall geological map. In the assessment of Dapaah-Siakwan and Gyau-Boakye (2000), the country is dominated by two major hydrogeological provinces:

- The Basement Complex composed of the Precambrian igneous and metamorphic rocks constituting about 54% of the landmass,
- The Paleozoic sedimentary basin which comprises the Voltaian sedimentary basin which underlies about 45% of the total landmass of Ghana.

The Cenozoic, Mesozoic, and Paleozoic sedimentary strata along the coast and the Quaternary alluvium along major stream courses constitute the remaining 1% of the hydrogeology of Ghana. These divisions have been used to describe the hydrogeology of Ghana for some time now, although the existing data suggest that the geological formations lumped together as the basement complex are significantly different in terms of their groundwater occurrence, well yield, and groundwater quality. The Birimian Province is made up of aquifers of the Lower and

Upper Birimian rocks, and Tarkwaian aquifers. The Pan African Province is made up of aquifers of the Buem and Togo Formations (Dapaah-Siakwan and Gyau-Boakye, 1998).

2.2 Mode of Occurrence of Groundwater

The occurrence of groundwater in all but the Coastal Sedimentary Province aquifers depends on secondary structures made up of fractures, veins and faults. The development of secondary permeability in these rocks is dependent on the nature, aperture, length, density, thickness and the degree of interconnection of the fractures (Atobrah, 1980) and in-filling of the fractures as well as the extent of weathering. The development of fractures and faults is a direct consequence of the cooling processes and the pressure release due to erosion, compressional and tensional activities during regional tectonic processes. In these rocks, the mode of occurrence of groundwater is basically linked with the nature and thickness of the zone, rock fracture, joints, quartz veins and pegmatites. Most of the quartz veins and pegmatites are fractured and to some extent brecciated as a result of brittle deformation as a consequence of Proterozoic Eburnean orogenic activities which affected them. The water-bearing and yielding capacities of these rocks depend on the extent of these secondary permeabilities (Banoeng-Yakubo 2000 and Banoeng-Yakubo, 2001).

Groundwater in the Crystalline Basement Provinces occurs mainly in the saprolite, saprock and in the fractured bedrock. The most productive zones in terms of groundwater in the Birimian Province comprise the lower part of the saprolite and the upper part of the saprock which usually complement each other in terms of permeability and storage (Carrier et al., 2008). The upper less permeable part of the saprolite can act as a semi-confining layer for this productive zone, 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 and Tarkwaian rocks display deeper seated weathering than areas underlain by the granitoids. In the articles presented by Banoeng-Yakubo (1989) and Norgbe (1998) three types of aquifers were identified in the basement aquifers. These are:

- The weathered rock aquifers, which are fracture related, the fractured quartz-vein aquifers and the fractured unweathered aquifers.
- In the Crystalline Basement aquifers, the saprolitic zone is a combination of the top soil, the underlying lateritic soil, the highly weathered zone and the moderately weathered zone.
- The saprock is the poorly weathered zone. Together, the saprolite and the saprock are the regolith.

In a recent assessment of the hydrogeology of Northern Ghana, a conceptual model was developed similar to what has been outlined (Carrier et al., 2008).

Borehole depths are varied in the Crystalline Basement Province aquifers (Carrier et al, 2008). This province is characterized by highly fractured sandstones, phyllites, greywackes, greenstones and schists. Many of them are crisscrossed by fractured quartz-veins and prolific aquifers have been encountered at an average depth of 25 m. The productive wells are completed in the moderately to poorly decomposed zones. The depth of weathering is dependent on the nature of the granitoids and the fissility in the rock. For instance, very productive and high-yielding aquifers are encountered in coarse-grained granites especially those traversed by fractured quartz-veins and depths of up to 60 m are not uncommon. It must be mentioned that the depths mentioned in this paper do not necessarily indicate the true depths of the aquifers. In Ghana, most boreholes were drilled for rural water supply and these boreholes are usually fitted with hand-pumps and their depths are dictated by their purpose. Most groundwater projects terminate drilling when sufficient water is obtained for rural water delivery. Depths of boreholes drilled through rocks of the Birimian and Tarkwaian Systems range between 35 m and 62 m with an average of 42m (Agyekum, 2004). Borehole depths in areas underlain by the granitoids are similar and range between 35 m and 55 m, with an average of 50 m (Carrier et al., 2008). In some areas the regolith is tapped at relatively shallow depths with relatively shallow hand dug wells.

Aquifer transmissivity of the productive zones of the Birimian and Tarkwaian Systems ranges between 0.2 m^2/d and 119m^2/d, with an average of 7.4 m^2/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 m^2/d and 40 m^2/d with an average of about 10 m^2/d. For the integrated aquifer systems in the Birimian and Tarkwaian Systems, borehole yields are generally low and range from 0.48 m^3/h to 36.4 m^3/h with a mean yield of 7.6 m^3/h. Differences in the degree of weathering within the granitoids probably account for the lower yields observed in these rocks, (Yidana et al., 2008|)

In the Voltaian Province, groundwater occurs in fracture zones and bedding planes since the primary porosity of some of these rocks was reduced due to consolidation and cementation. The hydrogeological properties of the larger Voltaian Province are varied and based on the degree of weathering and fracturing of the otherwise impervious rocks. Available data suggest that borehole yield within the Lower Voltaian sub-province ranges between 1 and 9 m^3/h with an average of about 6.2 m^3/h. On the basis of available data from drilling projects in this sub province, success rate for drilling prolific wells and boreholes is about 55%, (Yidana et al., 2008).

Success rate for drilling successful boreholes in the Middle Voltaian sub-province is about 56% and the average borehole yield is about 6.2 m^3/h. Borehole discharge characteristics at some locations within this sub province indicates artesian conditions at shallow depths (Yidana et al., 2008). In the Upper Voltaian sub-province, borehole yields range between 0.41 m^3/h and 9.0 m^3/h and average about 8.5m^3/h. Success rate for drilling successful boreholes in this is about 56%, (Yidana et al., 2008).

The average thickness of the regolith over the Voltaian sedimentary rocks is about 9 m. However, previous investigations in the Nanumba and West Gonja districts of the northern region of Ghana revealed average regolith thickness of 6 m and 11 m respectively. The relatively thin regolith can be explained by the relatively stable clay (shale) and quartz (sandstone) composition or by the fine texture or ductile nature of the sedimentary rocks found in the Voltaian Province (Carrier et al., 2008).

Deeper seated weathering may occur in areas underlain by arkose or arkosic sandstones such as the Middle Voltaian and are rich in K-feldspar and low temperature plagioclase feldspars. These minerals weather faster than quartz and clay minerals, Bannerman (1990). Underlying fracture systems are commonly developed at depths greater than 20 m below ground surface but on the average, required yields for rural water supplies are obtained above 100 m depth. Bannerman (1990) revealed that the most productive fracture zones occur between the depths of 13 m and 80 m with an average of 27 m.

Borehole data suggest that wells and boreholes in the Voltaian Province are slightly deeper than those in the Birimian. Borehole depths tabulated by Carrier et al. (2008) range between 45 m and 75 m with a mean depth of 55 m. Fractured rock aquifers in the Voltaian aquifers generally have a low to moderate productivity and overall transmissivity will range from 0.3 m^2/d to 267 m^2/d with a mean yield of 11.9 m^2/d.

Rocks of the Pan African Province comprise the Buem and Togo formations. The rocks are largely impervious but contain openings along joint, bedding, and cleavage planes. Where these openings are extensive, good supplies of groundwater can be developed from boreholes. Springs frequently occur along the flanks of hills where quartzites are in contact with argillaceous rocks of the valleys (Dapaah-Siakwan and Gyau-Boakye 2000). The yields of boreholes in the Buem formation range between 9 and 1260 l/min with an average and median of 100 and 78 l/min respectively.

The average depth of boreholes in the area is 60 m. On the basis of available well test data, aquifer transmissivity values range between 0.2 and 11.4 m^2/day. Specific capacities range from 0.04 m^3/h/m to 1.23 m^3/h/m with an average of 0.47 m^3/h/m. Dapaah-Siakwan and Gyau-Boakye (2000) reported an average yield in the Togo Series aquifers to be about 9.2 m^3/h, ranging between 0.72 m^3/h and 24.3 m^3/h. The highest yielding wells and boreholes in the Togo Series tap fracture zones. Rocks of the Pan African Province are among the most prolific aquifers in the country, and can be relied upon to deliver economic quantities of groundwater for various purposes. (Dapaah-Siakwan and Gyau-Boakye 2000).

The Coastal Sedimentary Province includes the Tano and Keta basin aquifers. The Tano basin comprises Cretaceous to lower Tertiary sedimentary rocks which include a thick section of alternating sand and clay with occasional thin beds of gravel and fossiliferous limestone. Limestones have been reported to have an oil and gas potential. Seepages of gas and oil have been reported in boreholes in the area. In the Cretaceous to lower Tertiary sediments, groundwater is obtained largely from the upper 91.4 m of the section. The average yield of the boreholes in this unit is about 12.6 m^3/h (Dapaah-Siakwan and Gyau-Boakye, 2000). Records of boreholes in the limestone aquifer in the Keta area indicate that the average yield of wells is about 13 m^3/h. Boreholes tapping the limestone aquifer in the Keta and surrounding areas have been reported to have a yield of about 49.5 m^3/h on the average and range from 45 m^3/h to 54 m^3/h.

2.3 Groundwater Chemicals Interpretation Techniques

2.3.1Graphical Techniques

The interpretation of groundwater chemistry can be done using graphical displays like piper diagrams, stiff patterns and diagrams, flow path observation (Mahlknecht et al., 2004). Mahlknecht et al. (2004) however noted that even though graphical representations are very helpful in the preliminary evaluation of ground water types and of the relationships between groundwater and lithology, the graphical display has the following setbacks;

The graphical display deals with limited number of chemical elements and therefore appears subjective in the interpretation as one would have to choose which element to represent (Güler et al., 2002).

Also, flows path configurations are only possible if selected samples intersect and this is only possible where there is an appropriate calibrated groundwater flow model of the study area (Parkhurst et al., 1996). Despite these inadequacies about the graphical method, graphical method remains a preferable technique for analyzing ground water chemistry for many. In Ghana, Yidana et al. (2009) used the technique to characterize the hydrochemistry of groundwater in northern Volta. The study revealed groundwater hydrochemistry is controlled by silicate and carbonate minerals and that cation exchange was observed and the geology appeared to have a great impact on the quality of water in the study area with low cation exchange effect.

Pelig-Ba (1998) used descriptive statistical methods to underscore that groundwater from some crystalline rocks in the Upper East Region indicate trace elements concentration were higher as compared to their concentrations found in natural water systems. Fianko et al. (2010) used the method to show that ground water in his studied area (Tema District) is fresh and generally suitable for resources.

Graphical Methods form one of the conventional approaches used in presenting chemical data of major ions that typifies groundwater. Major ions such as sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and sulphate (SO_4^{2-}) are represented in various graphs

The techniques are used to identify water samples with similar chemical composition and group them since samples with these similar characteristics often bear similar hydrologic background, originate from similar recharge areas, and have the same infiltration pathways and flowpaths in terms of climate and residence time (Güler et al., 2002).

The common methods include bar charts (Collins bar graph), pie charts, histograms and Schoeller semi-logarithmic graphs. The Schoeller semi-logarithmic diagrammatically presents the concentration of major ions of all the samples analyzed on a single semi- log sheet with the ions on the normal side and the concentration on the logarithmic side. The resulting plot is then visually analysed for patterns and deductions.

Yidana et al., (2010) used the averages of the chemical parameters in the four clusters of the Keta basin to plot Schoeller diagrams to observe that the differentiation in the cluster analysis is therefore associated with the EC values, which are dictated by the major influences in the hydrochemistry and that the static water levels do not appear to be correlated with salinities among the clusters defined.

2.3.2 Multivariate Statistical Analysis

Multivariate statistical analysis generally refers to a range of statistical techniques and methods which primarily involves data with several variables, with the objective of investigating the dependence relations between the involved variables (Hamdan, 2012). It is used to study the variations, relations, distributions of the hydrogeochemical data. Some of the multivariate techniques include Principal Component Analysis (PCA), Cluster Analysis (CA) and Factor Analysis (FA). These are effective techniques of manipulating, interpreting and representing data concerning groundwater pollutants and chemistry (Belkhiri et al., 2011).

Unlike graphical methods, multivariate statistical methods such as cluster and factor analyses provide a powerful tool for analyzing groundwater data for grouping into distinct hydrochemical zones. Multivariate statistical analysis has been successfully applied in a number of hydrogeochemical studies (Meng and Maynard, 2001; Güler et al., 2002; Güler and Thyne, 2004; Thyne et al., 2004; Helstrup et al., 2007; and Yidana et al., 2008a, 2008b). Although statistical associations do not establish cause-and-effect relationships, they provide helpful associations from which such relationships can be deduced (Yidana et al., 2012). Farnham et al. (2003) have applied multivariate statistical analysis to trace element chemistry of groundwater to help identify rock-water interaction processes and groundwater redox conditions.

Multivariate statistical technique has also been employed in this study to identify the different sources of solutes in groundwater (a) dissolution of calcium and magnesium carbonate minerals, (b) weathering of acid volcanic minerals, (c) alteration of manganese containing alkaline silicates, (d) leaching of halite deposits of meteoric origin, (e) contamination from agricultural and urban wastewaters, and (f) evaporative effects due to intensive irrigation (Mahlknecht et al., 2003).

Cloutier et al., (2008), applied two multivariate statistical methods, hierarchical cluster analysis (HCA) and principal components analysis (PCA) to a subgroup of the dataset which was made up of 144 samples and 14 parameters to evaluate their usefulness to classify the groundwater samples, and to identify geochemical processes controlling groundwater geochemistry. It was revealed that the following factors were recognized as influencing the evolution of groundwater: (1) geological characteristics including sedimentary rock type and till mineralogy; (2) hydrogeological characteristics represented by the level of confinement and the hydraulic gradient; and (3) the geological history of the area.

Yidana et al., (2006) applied HCA and PCA to assess the main controls on the chemistry of surface water resources from the Ankobra Basin and concluded that the hydrochemistry of the basin is controlled by the weathering of minerals and the decay of organic matter. Banoeng-Yakubo et al., (2009) also employed multivariate technique and mass balance approaches to study the main determinants of the hydrochemistry of groundwater in some sections of the Volta Region of Ghana. R and Q-mode hierarchical cluster analysis (HCA) were combined with factor analysis with principal components and varimax rotation, to determine field associations among the sample points, and their most possible sources of origin.

Principal Component Analysis is also a popular multivariate technique used for the understanding of large quantity of data involved in extended aquifer studies (Invernizzi and Oliveira, 2004). Khan (2011) used PCA and regression analysis to analysis hydrochemical data in the Ganja Basin in India. The PCA used in this study identified five factors that were responsible for the data structure explaining 83.49 % of the total variance of data set. The regression analysis showed that electric conductivity (EC) as an independent variable which could be used to measure carbonate (CO_3^{2-}), chloride (Cl^-), sodium (Na^+) and total dissolved solids (TDS). Further magnesium (Mg^{2+}) can be used to calculate the total hardness (TH) directly in the area.

Chen et al., (2006) used multivariate statistical analysis to investigate relationship among trace elements and factors controlling trace element distribution in groundwater. The study also attempted to investigate the data of trace elements in groundwater using multivariate statistical techniques such as principal component analysis (PCA), Q-mode factor analysis and cluster analysis where it came to a conclusion that multivariate statistical techniques are efficient ways to display complex relationship among many objects.

The grouping of objects such that objects fall into the some class is clustering. Cluster analysis comprises series of multivariate methods which are used to find true groups of data (Chen et al., 2006). Hierarchical clustering joins the most similar observation and then successively the next most similar observation. This type of cluster analysis is the most widely applied techniques in the earth science and Chen et al., (2006) also noted that, the attention of Q-mode factor analysis is devoted to interpret the inter-object relationship in a data set rather than the inter-variable relationship in a data set rather than the inter-variable relationship explored by the principal component analysis (PCA). Cosine θ coefficient of proportional similarity is the most widely use similarity measure in Q-mode factor analysis equation (Chen et al., 2006)

The multivariate statistical technique used for data reduction and for deciphering patterns within large sets of data is known as Principal Component Analysis (PCA). It is nothing more than the eigenvectors of a variance-covariance or a correlation matrix of the original data matrix. They may provide significant insight into the structure of the matrix not available at first glance and result may vary considerably depending on whether the covariance or correlation matrix is used when large differences exist in the standard deviation of the variable (Chen et al., 2006).

According to Chen et al., 2006, PCA was used to extract three independent factors which explained 93.2% of total variation and Q-mode factor analysis also generated three factors which gather accounted for 99.9% of the total variance. The three factor obtained in this way were rotated using the varimax procedure which could be more easily interpreted. The Q-mode factor analysis also described the relative proportions of these trace elements in groundwater samples. Cluster analysis also showed that the samples collected from the same well during different surveys, except for four well clustered together therefor concluded that the analysis of hydrochemical data using the multivariate statistical techniques such as PCA, Q-mode factor analysis and cluster analysis can give same information not available at the first glance, (Chen et al., 2006).

Amin and Subyani (2011) also used multivariate (Cluster and Factor) statistical analysis and spatial interpolation to assess groundwater contamination by toxic elements in Wadi Fatimah Western Arabian Shield, Saudi Arabia. They used Cluster and Factor Analysis in that study where R-mode is expected to depict relationships between variables, while Q-mode is to identify relationships between samples and factor analysis was also to examine the underlying patterns or relationships for a large number of variables and summarize information in a smaller set of factors or components for prediction purposes.

Amin and Subyani (2011), further explained how PCA was used in other studies to define the orthogonal linear transformation that transform the variables to a new coordinate system such that the greatest variance by any projection of the variables comes to lie on the first coordinate called the first principal component and the second greatest variance on the second coordinate.

Some results showed that some of the elements from the study were medium to high positively correlated to each other example Arsenic (As) was highly correlated with Lead (Pb), Aluminum (Al), etc., but Zinc (Zn) was totally uncorrelated with other elements. Three main groups were also verified using the Q-mode and R-mode cluster analysis each where the first cluster of the Q-mode showed a high similarity between the wells in the same geological formation, the second cluster originated from Basaltic formation and the third group belongs to the main stream of Wadi Fatimah.

2.3.3 The pH

pH is a water quality parameter which is defined as: pH = $-\log_{10}[H^+]$. Natural waters usually do not exceed the pH range 3-10, and in most cases remain between pH = 6 and 9. The pH of natural water is extremely important because it determines the solubility and chemical forms of most substances in water; for example, hydroxides of many metals are insoluble at higher pH's and less metal ion is available in the water unless hydroxide-complexes are formed (Essumang, 2000). Acidity and alkalinity are both inhibitory and destructive to bacteria, that is, bacteria can only survive in either neutral, mild acid or mild alkaline conditions. For example, the bacteria Escherichia coli (E. coli) is active within the pH range of 6-7 and in any artificial media, growth will seize at pH around pH 9 (Essumang, 2000).

2.3.4 Trace Elements

It has been observed that the reduced forms of Cr and V tend to form stronger organic complexes and be more particle reactive than their oxidized forms (Jeong-Yul, 2004). Adsorption of anoxic Cr and V species on metal oxides decreases with decreasing pH (Jeong-Yul, 2004). Johnson et al., (1992) discussed the cycling and speciation of Cr in a seasonally anoxic lake and found that chromate was the dominant dissolved species in oxic and suboxic in the presence of sulfide or ferrous iron. Chromate is slowly removed by adsorption onto settling particles while Cr (III) is colloidal reflecting its strong complexing ability with organic matter and particles (Yeong-Yul, 2004). In contrast to Cr and V, the work of Pierce and Moore (1982) indicates that As (III) and As (V) species have about the same affinity for amorphous iron oxyhydrocides and their adsorption decreases with increasing pH (Jeong-Yul, 2004).

The recycling of Mn and Fe in aquatic systems with variable redox conditions is complex. Davison (1993) pointed out that the distributions of Mn and Fe are influenced by redox conditions, the unique chemical characteristics of the metals, and physical mixing processes (Yeong-Yul, 2004 and references therein). The physical and chemical forms of Mn and Fe differ across oxic-anoxic interfaces. Within the oxic regions, both elements exist in their oxidized forms (Mn (IV) and Fe (III)) as insoluble metal oxyhydroxides. These solid phases tend to strongly adsorb trace metals. In anoxic environments, the elements are in their reduced forms (Mn (II) and Fe (II)) and exist as mobile metal ions, Mn^{2+} and Fe^{2+} (Jeong-Yul, 2004). The settling of Mn and Fe oxyhydroxides through an oxic-anoxic interface results in the reductive dissolution of the solid phases while the diffusion of dissolved Mn (II) or Fe (II) from reducing to oxidizing conditions can result in the precipitation of oxyhydroxides phases (Jeong-Yul, 2004 and references therein).

There are two important differences in the behaviour of Mn and Fe. First, Fe (II) has a faster rate of oxidation than Mn (II). This difference can result in a physical separation of Mn and Fe oxyhydroxieds because dissolved Mn (II) can be transported further from the redox boundary than dissolved Fe (II) before oxidation. Second, Fe tends to be more involved in the sulfur cycle than Mn. Iron sulphide phases can form possibly by the reaction of dissolved sulphide with iron oxyhydroxide (Jeong-Yul, 2004).

Fe concentrations are generally controlled by the solubility of ferri-hydrite. The Mn concentration increases as the Eh decreases, i.e. Mn solubilize as Mn^{2+}.

Increased Cl in solution can increase metal solubility due to formation of soluble chlorocomplexes of some trace metals. Chloride in solution increases the solubility of trace metals in the sequence Pb>Zn>Cu>Mn>Fe due to the vavrying strength of the metal-chloride complexes (Jeong-Yul, 2004). In oxic, strong acid system, the mobility of trace metals should be Mn>Zn>Cu>Pb and as such, results of theoretical studies in brines at pH < 6 without oxides present have shown similar mobility with Zn>Cu>Pb (Jeong-Yul, 2004).

2.3.5 Dissolved Organic Matter

The sources of Dissolves Organic Matter are largely effluent from solid disposal site, diaries slaughterhouses, tanneries, pulp mill residues, domestic sewerage and others.

Dissolves Organic Matter deprives aquatic life of dissolved oxygen. The dissolved organic matter uses up dissolved oxygen in water; they are oxidized by dissolved oxygen present in the water usually depleting the available oxygen in the water more rapidly. Also, a number of organic compounds are suspected carcinogens, and there is apparently a significant relationship between their presence and total cancer mortality (Essumang, 2000).

2.3.6 Tetraoxosulphate (IV), SO_4^{2-}

Sources of sulphate results from the oxidation of sulpide ores, gypsum, industrial wastes and decomposition of solid waste. It is commonly present in less than 1000 ppm except in streams and wells influenced by acid mine drainage, and as much as 20 000 ppm in some brines (Essumang, 2000). Sulphate combines with calcium to form an adherent heat retarding scale. More than 250 ppm are objectionable in water in some industries. Water containing about 500 ppm tastes bitter. High concentration of sulphates produces a laxative effect (Essumang, 2000).

2.3.7 Total Iron (Fe)

Sources of iron are, weathering of igneous rocks, metamorphic/sedimentary rocks amphibole, ferrous sulphide (FeS) iron pyrites, well casting , stoarage tanks, cast iron objects, and sewage. Generally, less than 0.5 ppm is present in fully aerated water. Groundwater having pH less than 8.0 may contain 10 ppm of iron (Essumang, 2000).

The iron is usually in the +2 oxidation state, but a concentration of more than 0.01 ppm is readily oxidized to the +3 oxidation state on exposure to air. Here, it precipitates as $Fe_2O_3.xH_2O$. The precipitation is pH dependent. Iron oxides cause turbidity and impart objectionable taste and colour to water. More than 0.2 ppm is objectionable for industrial uses because of its effect on food and drink (Essumang, 2000).

2.3.8 Dioxonitrate (III) NO_2^-

It is present in the atmosphere, in legume plant debris, animal excrement and nitrogenous fertilizers in soils and in (domestic) sewage (Essumang, 2000). In surface waters, which are not subjected to pollution, nitrite may be as much as 0.1 ppm but it is commonly absent.

The cause of “cyanosis” (blue water babies) in babies is due to the conversion of haemoglobin to methaemoglobin by nitrates - produced bacterial reduction of nitrate to nitrite (Essumang, 2000). This renders the haemoglobin incapable of transporting oxygen so that the characteristic blue colour and associated symptoms develop (Essumang, 2000 and references therein). Nitrates also react with amines and amides to form carcinogenic nitrosamines.

2.3.9 Trioxonitrate (V) NO_3^-

What is present in the atmosphere, in legume plant debris, animal excrement and nitrogenous fertilizers in soils and in (domestic) sewage (Essumang, 2000). In surface waters, not subjected to pollution, the concentration of nitrate may be as high as 5 ppm, but is commonly less than 1 ppm. Water containing large amounts of nitrate for example 100 ppm is bitter and may cause physiological distress. Water from wells containing more than 45 ppm has been reported to cause methaemoglobin in infants. The presence of nitrate in well water can cause "cyanosis" in babies (Essumang, 2000).

2.3.10 Chloride, Cl^-

Chlorides come from weathering of igneous rocks, sedimentary rocks, marine evaporates and rock salts. Its concentration is less than 10 ppm in humid regions: about 19 300 ppm in seawater and as much as 200 000 ppm in brines. A concentration in excess of 100 ppm imparts a salty taste. Food processing industries require less than 250 ppm. Textile processing, paper manufacturing and synthetic rubber manufacturing industries require less than 100 ppm (Essumang, 2000).

Chloride is often studied because it is extremely mobile, very soluble and chemically non-reactive (Jeong-Yul, 2004). In the Sydney region of Australia, Johnson (1981) explained that the substantial proportion of excess SO_4 and HCO_3 is due to urban runoff, derived from the dissolution of atmospheric dryfall (Jeong-Yul, 2004).

2.3.11 Electrical Conductivity

Electrical conductivity is a measure of dissolved salts in water. Dissolved solids or salts are obtained from pollutants that get into water column from the surrounding environment. The dissolved salts in water have a marked effect on the bacterial survival in water. An increase in the dissolved salts content, though different salts have different mobilities, results increase in the bacterial survival range. Thus, a measure of electrical conductivity of environmental water sample will give an inducation of the extent of pollution of the water with respect to bacteria. The acceptable EC of Ghana Environmental Protection Agency (EPA) of usable water should be less than 750 μS/cm (Essumang, 2000 and references therein).

2.3.12 Phosphate

This result from the breakdown of phosphates from inorganic fertilizer, soaps and detergent and effluents from food processing plants and sewage.

Phosphate PO_4^{3-} as an inorganic fertilizer displaces arsenic in the soil as a free ion, which dissolves in water bodies. Arsenic is very toxic and could result in death of human beings. It could also cause eutrophication and algal blooms (Essumang, 2000).

2.3.13 Sodium

The taste threshold concentration of sodium in water depends on the associated anion and the temperature of the solution. It is said that at a room temperature, the average taste threshold for sodium is about 200mm/l which has no health-based guideline value according to W.H.O, 2008.

Sodium (Na) is found in virtually all food (the main source of daily exposure) and drinking-water. It should be noted that some water softeners can add significantly to the sodium content of drinking-water (WHO, 2008).

2.3.14 Ammonium NH_4^+

Ammonium ion could be present in water from such sources as: Artificial fertilizers dissolution of ammonia gas in water, decomposition of refuse soil plant debris and domestic sewerage (Essumang, 2000). Ammonia is particularly toxic to fish and aids eutrophication. When bacteria act on ammonium/ammonia it is converted to nitrates and therefore have all the effects of both nitrites and nitrates.

2.3.15 Hydrochemical Facies

Facies (I): $Na + K – Cl + SO_4$

Its source is believed to be mainly sulphate dissolution as Na^+ and SO_4^{2-} are the main ions that form this facies (Vikram and Dhruv, 2010).

Facies (II): $Ca + Mg – HCO_3$. It is interpreted as a result of dissolution of carbonate minerals (calcite, dolomite and aragonite).

This can be attributed to the mixing process of different types of water. The dissolution of CO_2 and oxidation of sulphides are the two major sources carbonates, silicates and aluminosilicate minerals chemical weathering. The dissolution of carbonate rocks proceeds more rapidly than the silicate breakdown and as likely the mechanism of solute acquisition in the aquatic systems

(Vikram and Dhruv, 2010). The degradation of silicates incongruently generates a variety of solid phases (mostly clays) and dissolved species (Vikram and Dhruv, 2010). Relative high ratio of $HCO_3^-/HCO_3^- + SO_4^{2-}$ (>0.5) signifies carbonic acid weathering is proton producer in waters (Vikram and Dhruv, 2010).

2.3.16 Saturation Index

The potential for a chemical reaction can be determined by calculating the chemical equilibrium of water relative to the mineral phase. The equilibrium state of water with respect to a mineral phase can be determined by calculating a saturation index (SI) using analytical data (Vikram and Dhruv, 2010).

$$SI = \log_{10} \frac{IAP}{Ksp}$$

Where IAP = ion activity product, K_{sp} = solubility product at a given temperature.

Ar temperature 25°C, the SI relative to calcite (cc), dolomite (dol) and gypsum (gyp) are:

$$SI = \log IAP_{cc} - \log K_{cc} = \log IAP_{cc} + 8.5$$

$$SI = \log IAP_{dol} - \log K_{dol} = \log IAP_{dol} + 16.5$$

$$SI = \log IAP_{gyp} - \log K_{gyp} = \log IAP_{gyp} + 4.6$$

$$\log IAP_{cc} = \log [Ca^{2+}] + \log [CO_3^{2-}]$$

$$\log IAP_{dol} = \log [Ca^{2+}] + \log [Mg^{2+}] + 2\log [CO_3^{2-}]$$

$$\log IAP_{gyp} = \log [Ca^{2+}] + \log [SO_4^{2-}]$$

For these expressions a SI calcite value of 0 corresponds to calcite solubility in equilibrium state, while values of +1 and -1 corresponds to 10 times and 1/10 times saturation, respectively (Vikram and Dhruv, 2010). A positive SI specifies that the water is supersaturated with respect to the particular mineral phase and therefore incapable of dissolving more of the mineral and that, under suitable physic-chemical conditions, the mineral phase may precipitate. A negative index (SI) indicates under saturation condition and dissolution of the mineral phase is possible, while a neutral SI indicates equilibrium state with the mineral phase is possible. The precipitation of $CaCO_3$ and $CaMg(CO_3)_2$ can be assessed in terms of the SI, the saturation indices of the carbonate minerals positively show super saturation (precipitation) of dolomite (Vikram and Dhruv, 2010).

Dolomite: super saturation or close to equilibrium – SI limit > -0.5

Calcite: under saturation – SI limit < +0.5

2.3.17 Irrigation Indices

Physicochemical parameters that are analyzed to determine the suitability of water for irrigation include Kelley's Ratio (KR) by Kelley (1963) and described as:

$$KR = \frac{Na^{+}}{Ca^{2+} + Mg^{2+}} \qquad (2.1)$$

with all ionic parameters expressed in meq/L.

Another parameter is Residual Sodium Bicarbonate (RSBC) index of irrigation (soil) water. It is used to indicate the alkalinity hazard of soil. RSC index is used to find the suitability of water for irrigation in clay soils which has high cation exchange capacity. The RSBC is determined according to Gupta and Gupta (1987):

$$RSBC = HCO_3^- - Ca^{2+} \qquad (2.2)$$

where, RSBC and the concentration of the constituents are expressed in meq/L.

Sodium Adsorption Ratio (SAR). It is a measure of the suitability of water for use in agricultural irrigation, as determined by the concentrations of solids dissolved in the water. Although SAR is only one factor in determining the suitability of water for irrigation, in general, the higher the sodium adsorption ratio, the less suitable the water is for irrigation. The SAR is calculated by the following equation given by Richards (1954) as:

$$SAR = \frac{Na^+}{\sqrt{\left(\frac{Ca^{2+} + Mg^{2+}}{2}\right)}} \qquad (2.3)$$

where all the ions are expressed in meq/L.

Methods of Wilcox (1955) and Richards (1954) have been used to classify and understand the basic character of the chemical composition of groundwater, since the suitability of the groundwater for irrigation depends on the mineralization of water and its effect on plants and soil. Percentage sodium can be determined using equation (3.4) by Richards (1954) as:

$$Na\% = \frac{Na + K}{Ca + Mg + Na + K} \times 100 \qquad (2.4)$$

where all cations values are given in mg/L.

Permeability Index is a combination of the parameters such as hydraulic conductivity, permeability and intrinsic permeability of fluid movement. The permeability of rock is independent of fluid properties. Intrinsic permeability is related to hydraulic conductivity. The Permeability Index (PI) is estimated according to Doneen (1964).

$$PI = \frac{Na^{+} + \sqrt{HCO_3^{-}}}{Ca^{2+} + Mg^{2+} + Na^{+}} \times 100 \qquad (2.5)$$

where, all the ions are expressed in meq/L.

Stiff diagram is one of the ways of representing water types. It is graphical representation of water chemical analyses (Stiff, 1951). A polygonal shape is created from three or four parallel horizontal axes extending on either side of a vertical zero axis. Cations are plotted in milliequivalents per liter on the left side of the zero axis, one to each horizontal axis, and anions are plotted on the right side. Stiff patterns are useful in making a rapid visual comparison between water from different sources.

A Piper diagram is a graphical representation of the chemistry of a water sample or samples. The cations and anions are shown by separate ternary plots (Kehew, 2001). The apexes of the cation plot are calcium, magnesium and sodium plus potassium cations. The apexes of the anion plot are sulfate, chloride and carbonate plus bicarbonate anions. The two ternary plots are then projected up onto a diamond. The diamond is a matrix transformation of a graph of the anions and cations. In Piper diagrams the concentrations are expressed as %meq/L.

A Schoeller Diagram is a semi-logarithmic diagram of the concentrations of the main ionic constituents in water (SO_4, HCO_3, Cl, Mg, Ca, Na/K) in equivalents per million per kg of solution (meq/kg). An equivalent is the amount of anion or cation species needed to add or remove one mole of electrons from a system. Concentrations of each ion in each sample are represented by points on six equally spaced lines and points are connected by a line. The diagram gives absolute concentration, but the line also gives the ratio between two ions in the same sample. If a line joining two points representing ionic concentrations in a single sample is parallel to another line joining a second set of concentrations from another sample, the ratio of those ions in those samples are equal.

CHAPTER THREE

RESEARCH METHODOLOGY

3.1 Sample Collection

Secondary data for the dissertation was obtained from Community Water and Sanitation Agency (CWSA) in the Central Region of Ghana. Field work and sample collection done by hydrogeologists of CWSA covering a total of 64 boreholes; with 15 boreholes in the Cape Coast Municipality, 16 boreholes in Mfantseman Municipality and 33 boreholes in Abura-Asebu-Kwamankese District. Collection, transportation and preservation of water samples to the laboratory were conducted following standard methods reported by APHA (1998) and Richards (1954).

Physico-chemical parameters such as water temperature, pH, electric conductivity and the dissolved oxygen were all measured in the field with portable electronic instruments during the sampling.

3.2 Chemical Analysis

Collected samples were analyzed at the water quality laboratory of CSIR-Water Research Institutes. All the chemical parameters namely Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-, F^- and Fe^{2+} were analyzed in the laboratory following internationally accepted procedures and standards, APHA (1998)

3.3 Tools for Data Analysis

Computer based programmes were used in water quality analysis. These include AquaChem 5.1, and HydroChem 2.0, among others. AquaChem is a fully-integrated software package developed specifically for graphical and numerical analysis of geochemical data sets. AquaChem features a powerful database that can be customized and configured to include an unlimited number of attributes per sample and a built-in database of inorganic parameters that are commonly-used for geochemical analyses, calculations and plotting. AquaChem's graphical plotting techniques include Piper, Stiff, Durov, Schoeller and ternary diagrams, radial plots, scatter graphs, frequency histograms and pie charts (AquaChem v.5.1Demo Tutorial, 2012).

In addition, AquaChem features a graphical interface to the popular geochemical modeling program PHREEQC for calculating equilibrium concentrations (or activities) of chemical species in solution and saturation indices of solid phases in equilibrium with a solution. AquaChem, is one of the most powerful tools available for anyone dealing with the interpretation, analysis and modeling of simple or complex aqueous geochemical data sets.

CHAPTER FOUR

4.0 RESULTS

4.1 Hydrogeochemical Data

The results from the analysis of the various hydrogeochemical parameters of groundwater samples from the 64 borehole stations are presented in Table A.1. The code CC (CC1 to CC15) represents boreholes from Cape Coast Municipal; those with MF (MF16 to MF31) are from Mfantseman District while the group from Abura Asebu Kwamankese District (AA) has codes from AA32 to AA64.

4.2 Hydrogeochemical parameters of groundwater

The hydrogeochemical parameters of groundwater quality data were statistically analyzed and summarized as presented on Table 4.1. For the physical parameters, pH ranges from 2.3 to 11.7 with an average of 6.5. EC ranged from 2.6 to 9760.0 with a mean value of 1288.6 µS/cm. The range values of TH and TDS are 16.0 to 1900.0 and 18.0 to 5368 respectively with their mean being 326.9and 754.0 mg/L. The order of abundance of the cations concentration is $Na^+>Ca^{2+}>Mg^{2+}>K^+$ while those of the anions is $Cl^->HCO_3^-> SO_4^{2-}$. The ranges of the cation concentrations are Na^+ (4.50 to 1366.0), Ca^{2+} (4.01 to 321.0), Mg^{2+} (0.9 to 335.0), and K^+ (1.3 to 80) with mean values of 167.4, 63.2, 43.1 and 14.4 mg/L respectively. The concentrations of the anions on the other hand indicate that Cl^-, HCO_3^- and SO_4^{2-} ranged from 7.7 to 3216.0, 0 to373.0 and 2.69 to 435.0 with mean values of 323.4, 134.0 and 14.5 mg/L respectively. For the physical parameters, pH ranges from 2.3 to 11.7 with an average of 6.5. EC ranged from 2.6 to 9760.0

with a mean value of 1288.6 µS/cm. The range values of TH and TDS are 16.0 to 1900.0 and 18.0 to 5368 respectively with their mean being 326.9and 754.0 mg/L. For the trace metals, Iron has values ranging from 0.01 to 9.8 mg/L with a mean value of 0.7 while Manganese is within the range of 0.01 and 3.1 mg/L with 0.5 as the mean.

Table 4.1: Summary of Hydrogeochemical Data Groundwater

Parameters	Average	Sta. Dev.	Range in Samples	No. of samples outside MPL
pH	6.46	1.05	2.26 - 11.7	36
EC	1288.63	1646.40	2.6 - 9760.0	12
TDS	753.97	993.62	18.0 - 5368.0	18
Na	167.36	263.97	4.5 - 1366.0	14
K	14.38	16.59	1.3 - 80.0	0
Ca	63.22	71.77	4.0 - 321.0	6
Mg	43.10	71.07	0.9 - 335.0	4
HCO_3	134.01	81.42	0.0 - 373.0	6
Cl	323.37	592.79	7.7 - 3216.0	18
SO_4	83.09	113.99	2.7 - 435.0	7
NO_3	4.07	4.86	0.1 - 23.4	0
Fe	0.68	1.55	0.01 - 9.8	10
Mn	0.45	0.59	0.01 - 3.1	39
TH	326.87	409.51	16.0 - 1900.0	12
TA	121.31	102.6	8.0 - 726.0	0
F	1.20	0.95	0.01 - 3.4	11

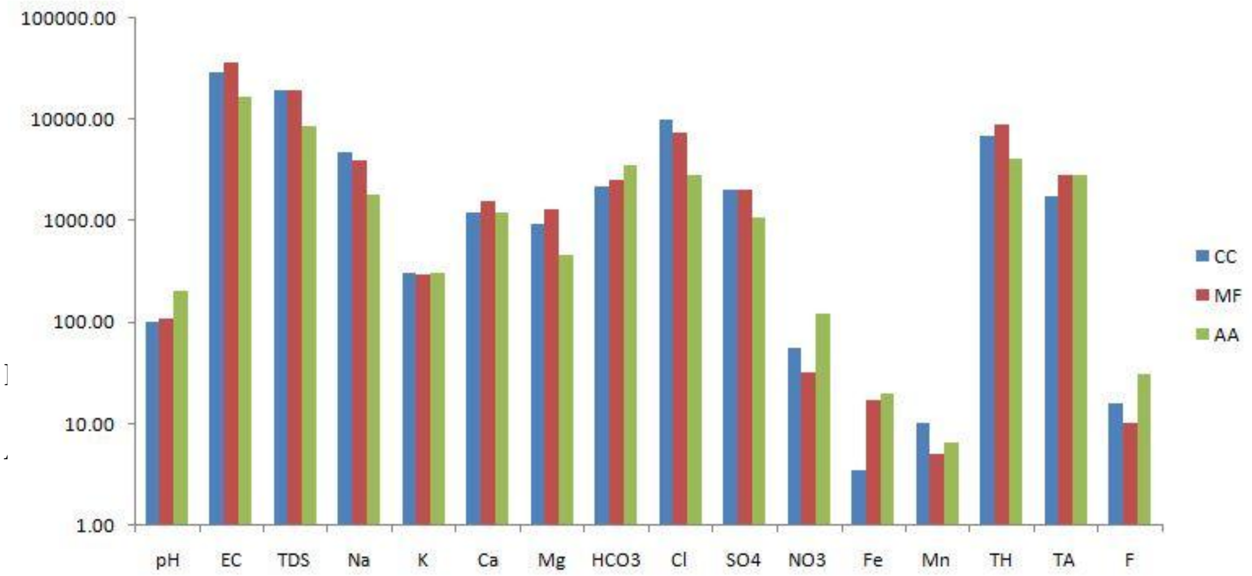

Fig 4.1: Bar graph showing summary of the parameters from the study area.

The summary of the parameters from the various study areas (CC, MF and AA) are represented in Fig 4.1. It can be seen that groundwater samples from the study area varied widely that it is difficult to observe a specific pattern, as to which area indicated the highest or lowest values compared to others. Therefore the mean quality showed that parameters are similar in all the areas.

4.3 Groundwater Quality for Domestic Purposes

4.3.1 Physical Parameters

The physicochemical parameters used in evaluating water quality are shown in Table 4.3. The minimum and maximum values of groundwater samples from the study area have also been given. The pH values of groundwater samples ranged from 4.9 to 7.7 with an average of 6.3 mg/L as shown on Table 4.1. From Table 4.2, 36 samples nearing 56.3% of the groundwater samples had pH values below the acidic limit of 6.5. Total Hardness of groundwater samples in the area relates to the quality of water and suitability for washing/bathing, that is, ability of the water to lather easily with soap. The hardness values ranged from 16.0 to 1900.0 mg/L. From the results in Table 4.2, 21.9% (14 samples) had hardness values beyond the maximum permissible limit of 500 mg/L for drinking water by Ghana Standards Board and WHO (2004). It can also be observed from Table 4.2 and Fig 4.2 that 35.9% of water samples are soft, 25% are moderately soft and 10.9% is slightly hard. On the other hand, 6.3% of samples are hard and 21.9% are very hard.

Table 4.2: Suitability for Washing based on Hardness (WHO, 2011)

Total Hardness as CaCO3 (mg/l)	Water Class	Number of Samples	Percentage
0 – 100	Soft	23	35.9
100 – 200	Moderately Soft	16	25
200 – 300	Slightly Hard	7	10.9
300 – 400	Moderately Hard	0	0.0
400 – 500	Hard	4	6.3
>500	Very Hard	14	21.9

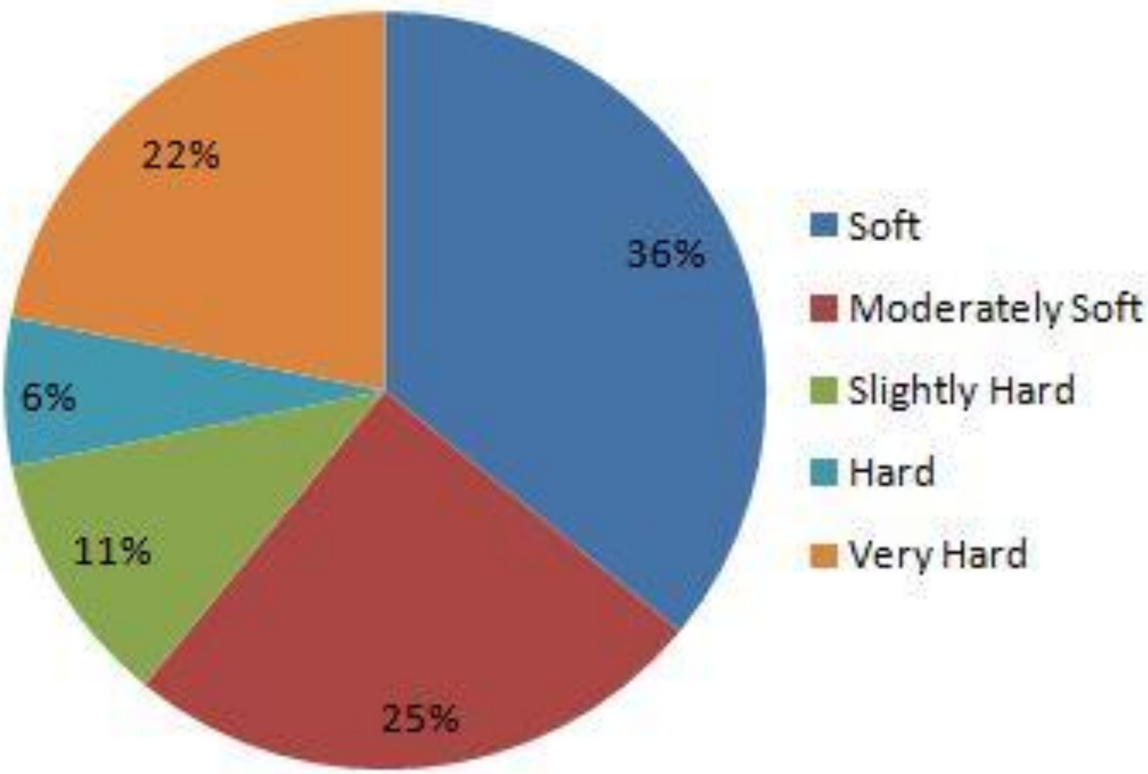

Fig 4.2: Suitability for Washing/Bathing based on Hardness (WHO, 2004)

The TDS concentration ranges from 18.0 to 5368.0 with 148.2 mg/L as the average, as shown in Table 4.1. According to groundwater classification based on TDS by Fetter (1990), 46 water samples representing 71.9% are fresh water type while the rest 18 samples (28.1%) are brackish water type as illustrated by Table 4.3.

Table 4.3: Classification of Groundwater based on TDS (Fetter, 1990)

Total Dissolved Solids (mg/L)	Classification	Number of Sample	Percentage
0 – 1000	Fresh water type	46	71.9
1000 – 10000	Brackish water type	18	28.1
10000 - 100000	Saline water type	0	0.0

4.3.2 Ions and Metals

Whereas the concentration of Na^+ in the groundwater samples ranged from 4.5 to 1366 mg/L, that of K^+ ranged from 1.3 to 80.0 mg/L (Table 4.1). The bar chart, Fig 4.4, is illustrative of the percentage contribution of the sum of individual cations and anions in the samples.

Ca^+ and Mg^+ originate from natural such as like granitic terrain which contains large concentration of these elements (Tikle et al., 2012). In this study, the values of Ca^+ ranged from 4.0 to 321.0 with an average of 24.4 mg/L while that of Mg^{2+} was from 0.9 to 335.0 with mean of 6.9 mg/L (Table 4.1). Ca^{2+} is the dominant cation with 43% of the total sum while Mg^{2+} consisted of 21% (Fig 4.2).

The presence of Sulphate (SO_4^{2-}) in drinking water can cause noticeable taste, and very high levels might cause a laxative effect in unaccustomed consumers (WHO, 2011). Taste impairment varies with the nature of the associated cation, as it is found in small quantities in groundwater.

In this study, Fig 4.3 shows that SO_4^{2-} constituted only 9% of the total major anions. The anion has values ranging from 2.69 to 435 (Table 4.1) with 7 samples (representing 10.9%) which are above the 250 mg/L limit recommended by WHO (2011).

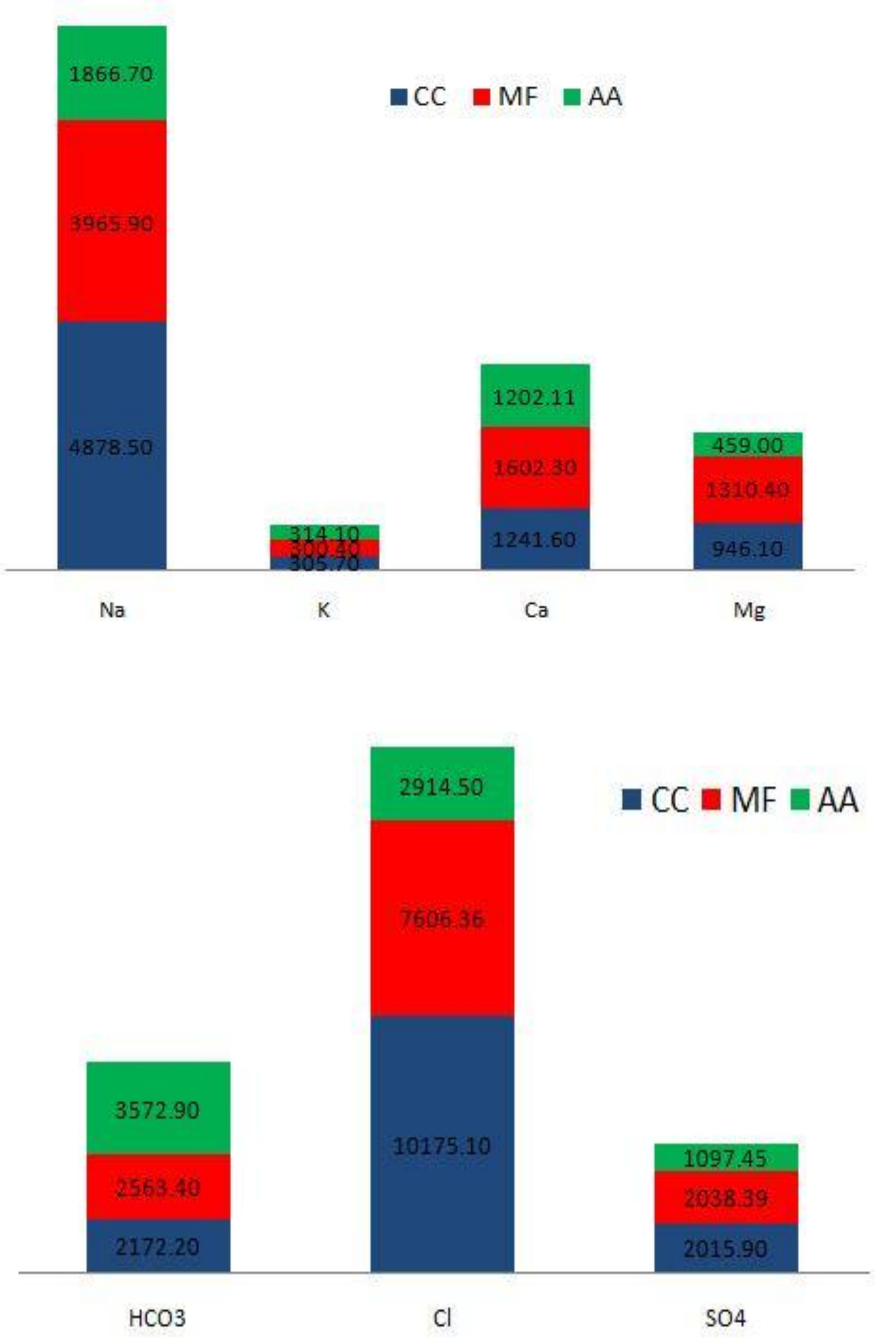

Fig 4.3: Bar Charts representing composition of the Major Cations and Anions

From Table 4.1, concentration of chloride in the groundwater samples ranged from 7.7 to 3216 mg/L, and 18 samples (nearing 28.1%) are far above the Ghana Standard Board and WHO (2011) most desirable and maximum allowable limits of 300 mg/L in drinking water. In the study area its contribution to total concentration of anions is very high (Fig. 4.3). A high concentration of Chloride (Cl-) gives a salty taste to water and beverages (WHO, 2011).

HCO_3^- concentration in the study area extended from 0 to 373 mg/L as evident in Table 4.1. Approximately 9.4% (6 samples) of the sampling stations have values exceeding the allowable limit of 240 mg/L set by the WHO (2011) guidelines for drinking water.

Concentrations of Fluoride (F^-) in samples in the study area ranged from as low as 0 to as high as 3.39 mg/L (Table 4.1). The study area recorded 11 samples (representing 17.2%) which have values beyond the threshold of 1.5 mg/L.

The trace Metals include Iron (Fe^{2+}) and Manganese (Mn). For Mn, as many as 39 samples representing about 60.9% were found to be above the WHO (2011) and Ghana Standards Board recommended maximum allowable limit of 0.1 mg/L in potable water. The 39 samples with their respective Mn values can be found in Table A.1. The values found in the study are between 0 and 3.3 (Table 4.1). Fe^{2+} concentration in the samples varied from 0 to 9.8 mg/L (Table 4.1). About 15.6% of all the groundwater samples (10) had elevated Fe^{2+} levels above WHO (2011) maximum recommended limit of 1 mg/L for drinking.

4.3.3 Processes Controlling the Hydrochemistry

The mechanisms responsible for controlling groundwater chemistry of the study area are shown by the relationship among the cations and anions. The average correlation co-efficient of Na^+ vs. Cl^- is 0.96 in Fig 4.4a indicating all samples plotting along the equiline. Ca^+ vs. HCO_3^- has almost all samples locating above the equiline in Fig 4.4c. Similarly, the bi-plots of the combination of K vs. SO_4 and Ca+Mg vs. HCO_3+SO_4 (Figs 4.4b and 4.4d) show majority of samples plotting above the equiline in each case. Fig 4.5 also shows the relationship between alkali and alkaline earths in the samples.

Mechanisms controlling groundwater chemistry and geo-environmental conditions have a marked influence on groundwater quality. Hydrogeochemical parameters relevant to the water quality explain the relationship of water chemistry to aquifer lithology. Such relationship would help not only to explain the origin and distribution of dissolved constituents but also to indicate the factors controlling groundwater chemistry (Chitradevi and Sridhar, 2011). It is a generally accepted fact that there is a close relationship between water composition and aquifer properties (Gibbs, 1970).

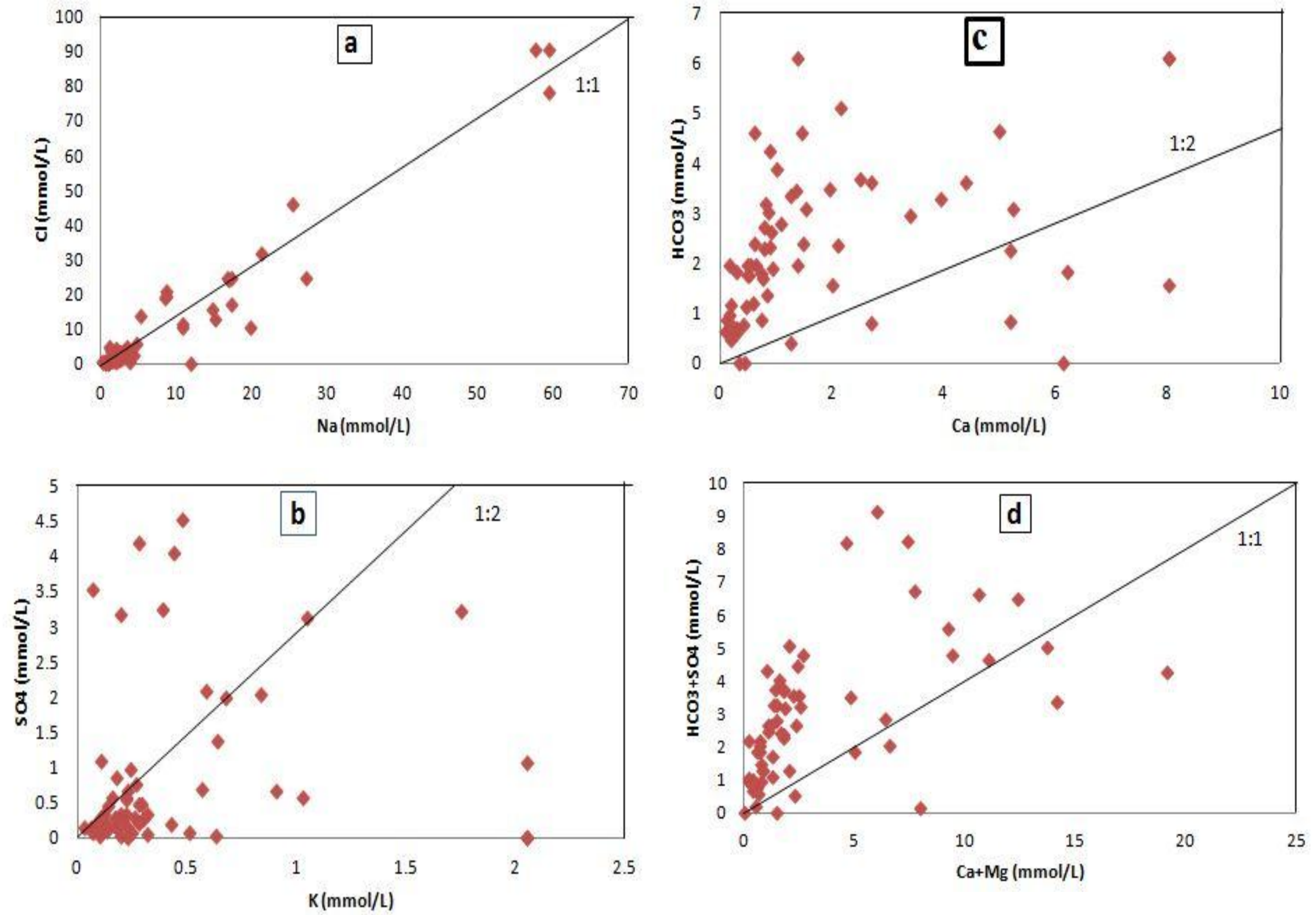

Fig 4.4: Bi-plots showing processes Controlling Hydrogeochemistry

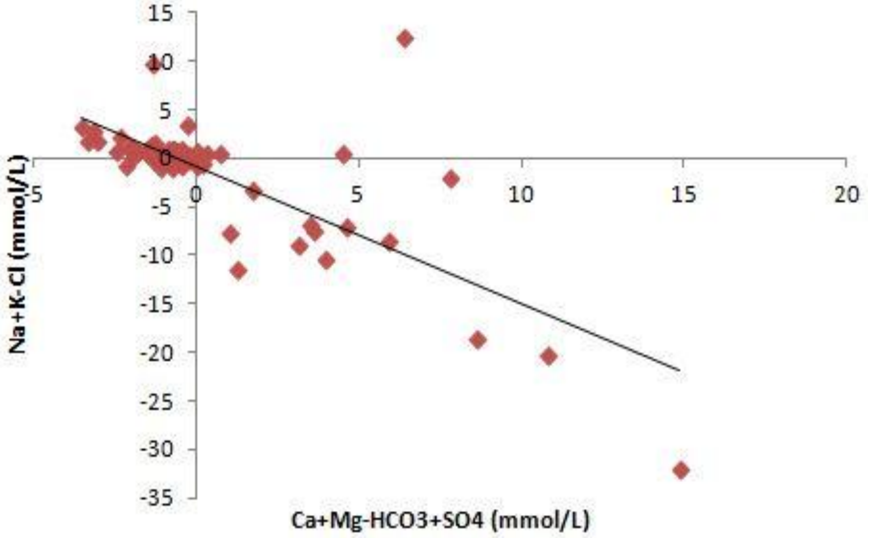

Fig 4.5: Scatter plot of alkali vs. alkaline earth elements showing processes controlling Hydrogeochemistry

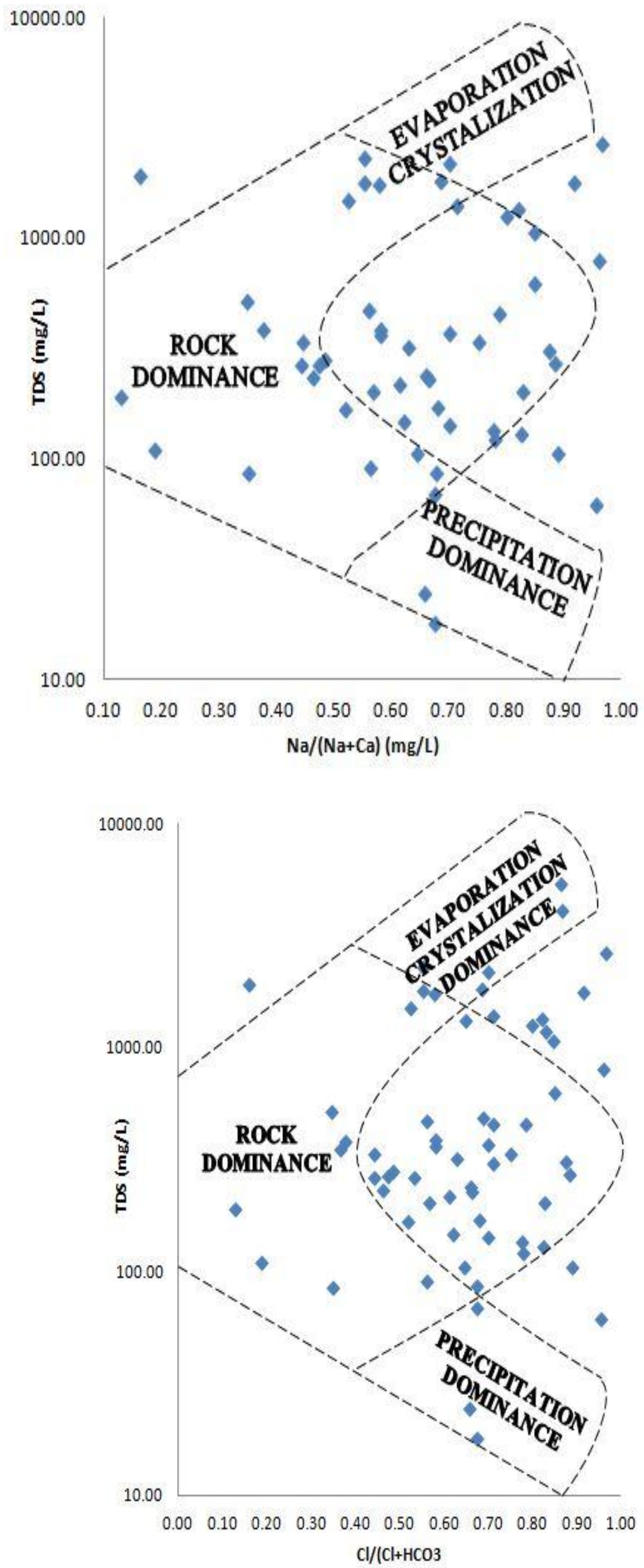

Fig 4.6: Gibbs Diagram representing Mechanisms governing Groundwater Chemistry (Gibbs, 1970)

4.3.4 Hydrogeochemical Facies

Piper Diagram (Fig 4.7) shows that the general dominant water type of the study area is Na-Cl, and the values obtained from the physicochemical analysis of groundwater samples indicated that the dominant cation in the area is Na^+ and the anion is Cl^-. The study also showed in Figs 4.8 that samples obtained from CC and MF produced Na-Cl groundwater type (Figs 4.8a and 4.8b), while those from AA gave rise to Na-Ca-Cl water type (Fig 4.8c).

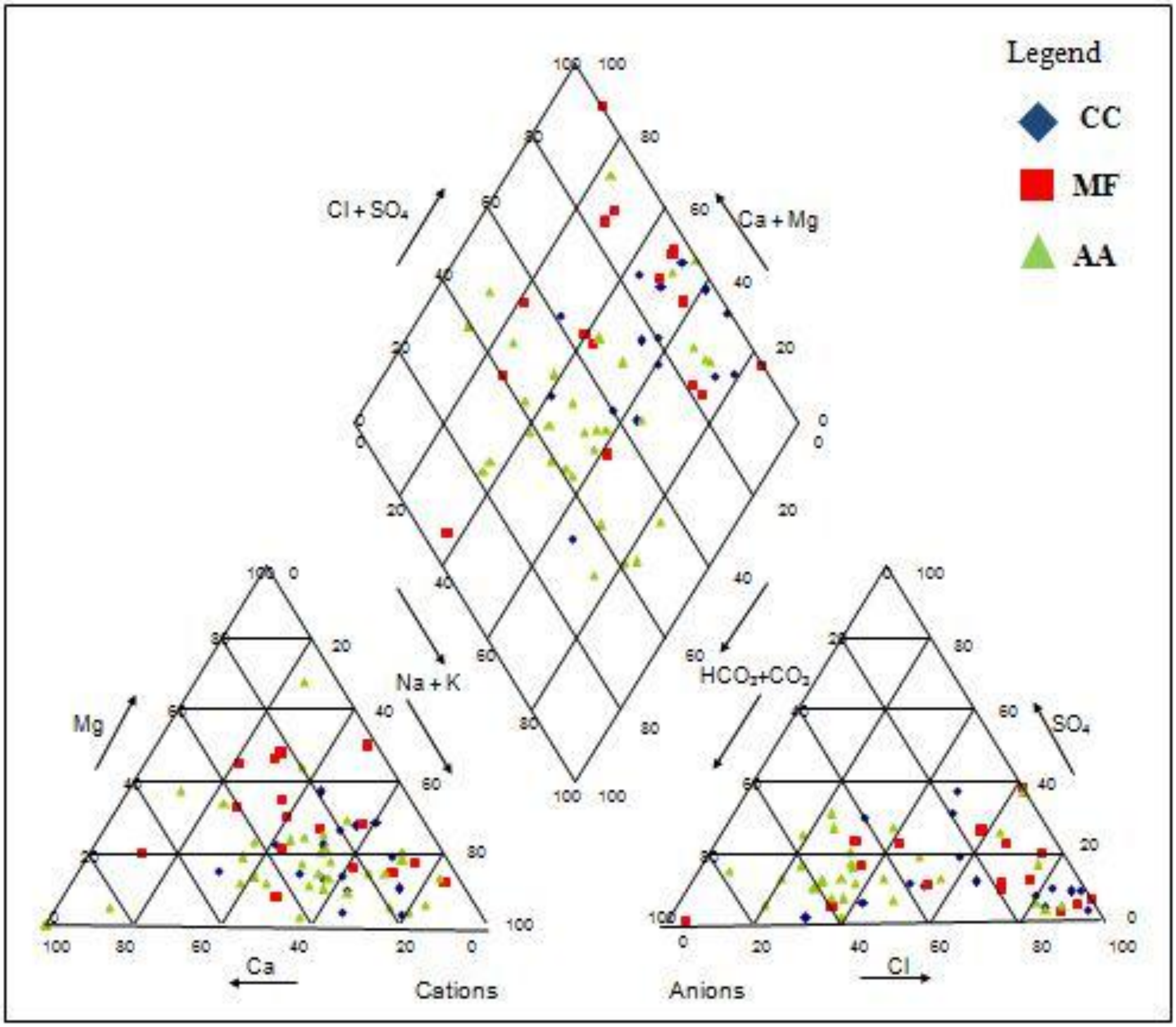

Fig 4.7: Hydrogeochemical facies of groundwater in Piper Diagram

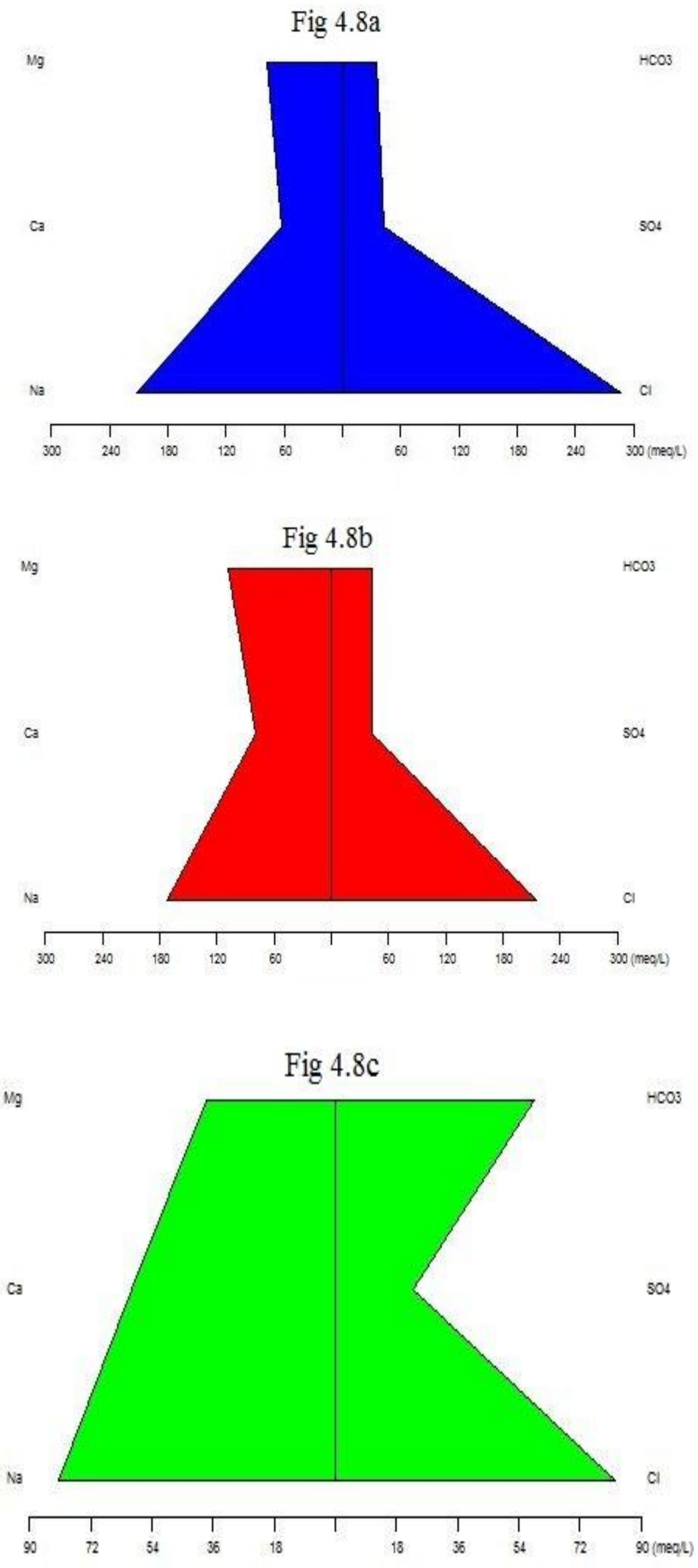
Fig 4.8a

Fig 4.8b

Fig 4.8c

Fig 4.8: Stiff diagrams illustrating Water Type in CC, MF and AA Sample Station

4.4 Quality Assessment of Groundwater for Irrigation Purpose

Salinity and indices such as, sodium absorption ratio (SAR), sodium percentage (%Na), residual sodium bicarbonate (RSBC), magnesium adsorption ratio (MAR), and permeability index (PI) are important parameters for determining the suitability of groundwater quality for agricultural use. Electrical Conductivity (EC) and Sodium (Na^+) also play a vital role in determining suitability of water for irrigation. All the calculated salinity indices values (Table A2) are expressed in milliequivalent per litre (meq/L) except values of TDS and TH which are in mg/L and EC in μS/cm.

Table 4.4: Summary of Salinity Indices of Samples

Parameter	SAR	RSBC	KR	%Na	EC	TDS	TH
Unit	(meq/L)			%	(μS/cm)	(mg/L)	
Minimum	0.00	-14.49	0.00	0	2.60	18.00	16.00
Maximum	16.05	3.37	5.37	84.42	9760.00	5368.00	1900.00
Mean	3.62	-1.03	1.30	50.55	1288.63	753.97	326.87
Std. Dev.	3.80	3.90	1.23	20.01	1912.28	1122.04	445.08

The EC and SAR usually combine to indicate the salinity level of water. In this research work, the values of EC and SAR ranges from 2.6 to 9760 and 0 to 16.1 with an average value of 1288.63 μS/cm and 3.6 meq/L respectively. The SAR is calculated using equation (3.3) given by Richards (1954). The classification of groundwater samples from the study area with respect to EC (Salinity Hazard) is represented by Table 4.5 and that of SAR (sodium hazard) is in Table 4.6.

Table 4.5: Classification of Groundwater samples based on Salinity Hazard (modified to accommodate values < 100 µS/cm)

Salinity Hazard Class	EC (µS/cm)	Water Class	Number of Samples	Percentage of Samples
C1	< 250	Low	12	19.0
C2	250 – 750	Medium	21	32.3
C3	750 -2250	High	7	11.0
C4	>2250	Very High	24	37.5

Table 4.6: Classification of Groundwater based on USSL Sodium Hazard for Irrigation

Sodium Hazard Class	SAR (meq/l)	Water Class	Number of Samples	Percentage of Samples
S1	<10	Low	59	92.2
S2	10 – 18	Medium	5	7.8
S3	18 – 26	High	0	0.0
S4	>26	Very High	0	0.0

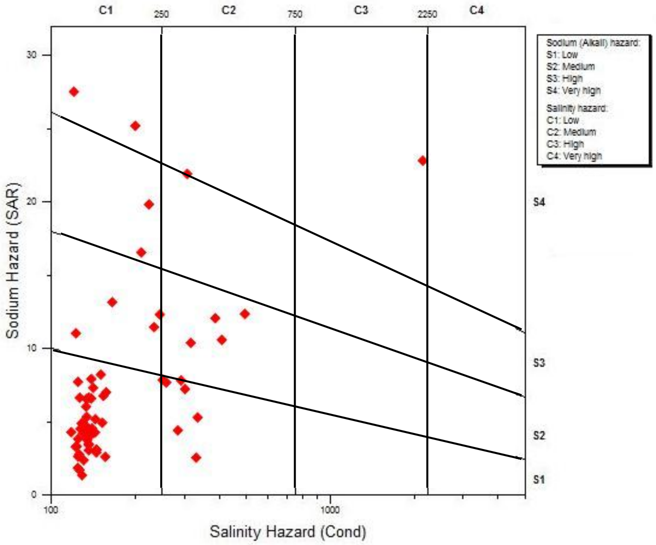

Fig 4.9: Assessment of the irrigation quality of water from the study area using the Wilcox (1955) methodology.

According to the US Department of Agriculture, water having more than 2.5 meq/L of RSBC is not suitable for irrigation purposes. The RSBC value ranges between -14.5 and 3.4 with a mean value of -1.0 meq/L (Table 4.4). A bar graph (Fig. 4.10) shows the classification of irrigation water based on RSBC. RSBC values of samples were determined using equation (3.2), where all ions were expressed in meq/L.

Table: 4.7: Groundwater quality for Irrigation Based on RSBC

RSBC (meq/L)	Water Categories	Number of Samples	Percentage of Samples
<1.25	Safe	55	85.9
1.25 – 2.5	Moderately Suitable	6	9.4
>2.5	Unsuitable	3	4.7

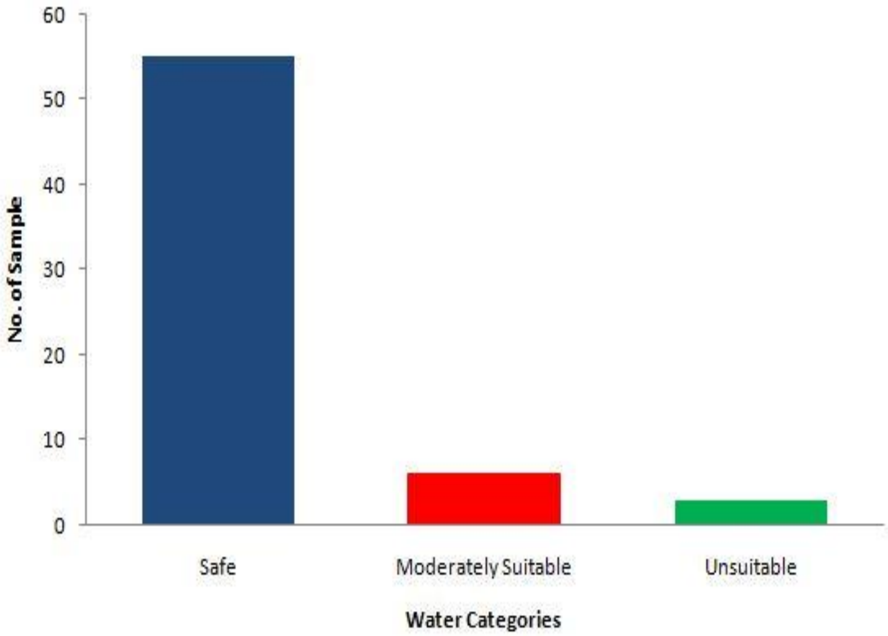

Fig 4.10: A bar chart of Groundwater quality for Irrigation Based on RSBC

The percentage sodium values of groundwater samples in the study area vary from 0 to 84.4 with an average value of 50.6% (Table 4.4). These values were determined using equation (3.4) by Richards (1954). It can be observed from Fig. 4.11 that 40 water samples (62.6%) are considered 'excellent to good', 2 and 8 samples representing 3.1 and 12.5% are 'good to permissible' and 'permissible to doubtful' respectively for irrigation purposes.

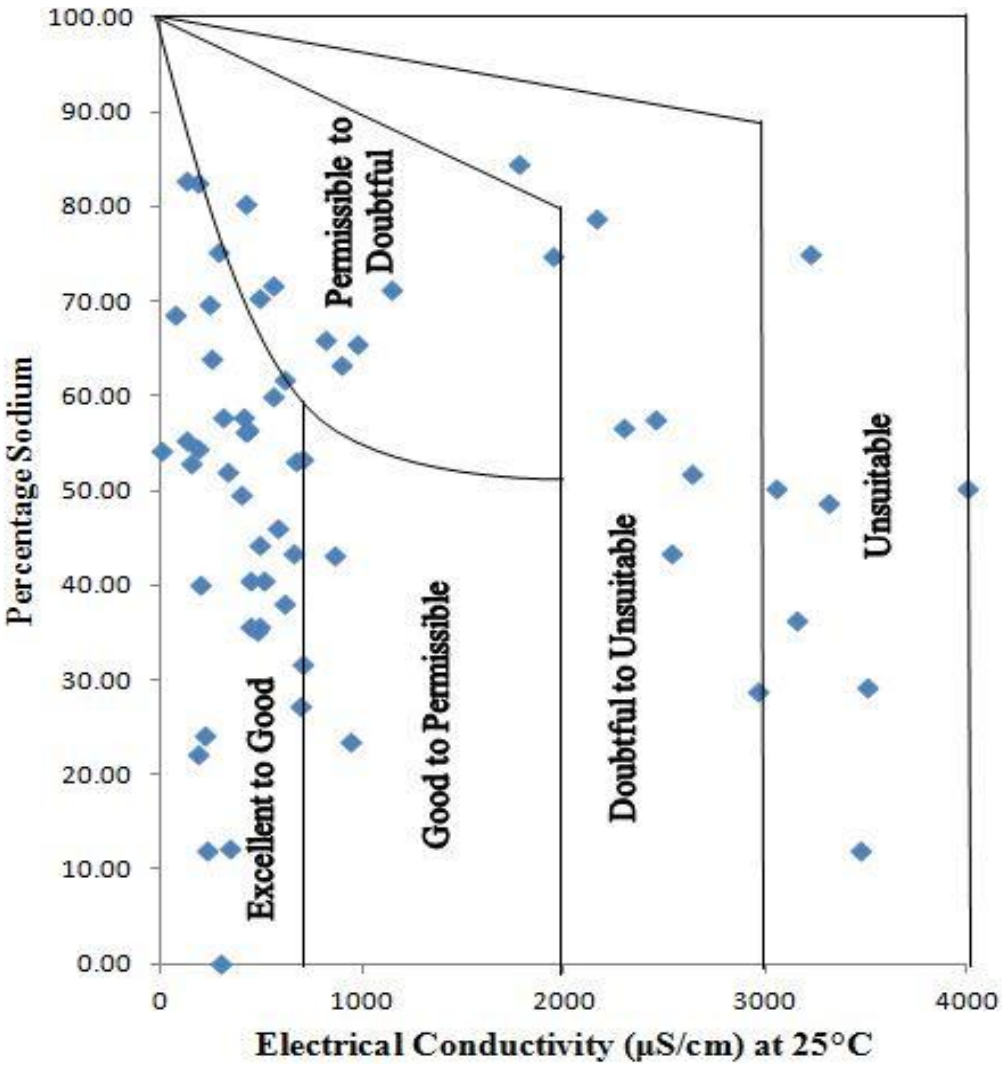

Fig 4.11: Groundwater Suitability for Irrigation based on Na% and EC (Wilcox, 1955)

Kelley Index Ratio (KR) is used for the classification of water for irrigation purposes. The KR values computed for the study area ranged from 0 to 5.37 with mean value of 1.3 meq/L (Table 4.4). Sodium measured against calcium and magnesium was considered by Kelley (1963) for calculating KR using equation (3.1) where, all the ions are expressed in meq/L.

Table 4.8 represents the nature of TDS in the analyzed water samples in the study. According to Obiefuna and Sheriff (2011), high levels of TDS in the form of salts of calcium, magnesium, sodium and potassium present in irrigation water poses dangers to the health of plants.

Table 4.8: Classification of TDS of studied samples according to Robinove et al., (1958)

TDS (mg/L)	Classification	Number of Samples
<1000	Non saline	46
1000 – 3000	Slightly saline	16
3000 – 10000	Moderately saline	2
>10000	Very saline	0

CHAPTER FIVE

5.0 DISCUSSION

According to Al-Amry (2008), the quality of water is very important to mankind, because it has a direct link with human welfare. The data on chemistry of the groundwater have been used for the evaluation of quality of water for drinking and irrigation purposes. The water to be used for drinking purposes must meet very high standards of physical, chemical and biological purity. Certain minimum quality parameters for this requirement have been suggested by World Health Organization (WHO, 2011).

5.1 Groundwater Quality Assessment for Domestic Purposes

5.1.1 Physical Parameters

The pH values of groundwater samples from Table 4.1 show that 36 samples out of 64 had pH values below the acidic limit of 6.5 (WHO, 2011). Some of these samples are CC7 (5.9), MF28 (2.3) and AA50 (4.8) among others. This implies that water from these wells is too acid for human consumption, which may pose health problems such as acidosis (Ackah et al., 2011). The low pH levels may be due to high rich-mineral rocks such as carbonate and gypsum making up the aquifers, from accidental spills, treatment breakdowns and insufficiently cured cement mortar pipe linings or cement mortar linings applied when the alkalinity of the water is low . EC ranged from 2.6 to 9760 with a mean value of 1288.6 µS/cm. Very large variations in the electric conductivity may be attributed to variation to total dissolved solids. The high conductivity in some of the samples is likely due to prolonged and intensive agricultural practices and geological conditions acquiring high concentrations of the dissolved minerals (Ramesh and Elango, 2012).

Even though no harmful effects are caused by EC, it gives salty taste to drinking water in areas where chloride is high (WHO, 2011).

The TDS concentration on the other hand, ranges between 18.0 and 5368.0 with 148.2 mg/L as the average (Table 4.1). The groundwater in the study area falls under fresh (TDS<1000 mg/l) to brackish (TDS>1000 mg/l) types of water (Freeze and Cherry 1979). Almost 72% (46 samples) of groundwater is classified as fresh whilst 28% of samples is brackish water (Table 4.3 by Fetter, 1990). The brackish nature of the 28% of samples may be caused by the high concentration levels Ca2+ and HCO3- from the weathering of granite (Ananthakrishnan et al., 2012). Based on total dissolved solids, groundwater is classified into desirable for drinking (up to 500 mg/l), and permissible for drinking (500–1,000 mg/l).

The hardness values ranged from 16.0 to 1900.0 mg/L. WHO (2011). Based on TH, groundwater quality ranges from soft to very hard. From the results in Table 4.1, 14 samples (21.9%) have hardness values beyond the maximum permissible limit of 500 mg/L for drinking water by (WHO, 2011). Total Hardness of groundwater samples in an area relates to the quality of water and suitability for washing/bathing, that is, ability of the water to lather easily with soap (Ackah et al., 2011). The hardness in current study can be adduced to from sedimentary rocks seepage and runoff (Milovanovic, 2007; www.ghanadistricts.com).

5.1.2 Correlation and Trend line Analysis

According to Chitradevi and Sridhar (2011) the major ions that contribute to groundwater chemical budget are Ca^{2+}, Mg^{2+} Na^{+}, K, Cl^{-}, HCO_3^{-}, and SO_4^{2-}. From Figs. 5.1a, 5.1b and 5.1c it is revealed that Ca^{2+}, Mg^{2+} and Na^{+} produce respectively 0.8, 0.9 and 0.8 correlation co-efficient (very strong relationship and linearity) with TDS. The calculated correlation co-efficient of 0.8 and 1.0 are obtained for TDS vs. SO_4^{2-} and Cl^{-}, respectively, showing very strong relationship and linearity. HCO_3^{-} on the other hand indicates a relatively weak linear relationship.

Trend line diagrams depicting these relationships are Figs. 5.1f, 5.1e and 5.1d respectively. The very strong correlation shown throughout the study area between TDS and Ca^{2+}, Mg^{2+} and Na^{+} depicts that the nature and origin of these ions would be the same source.

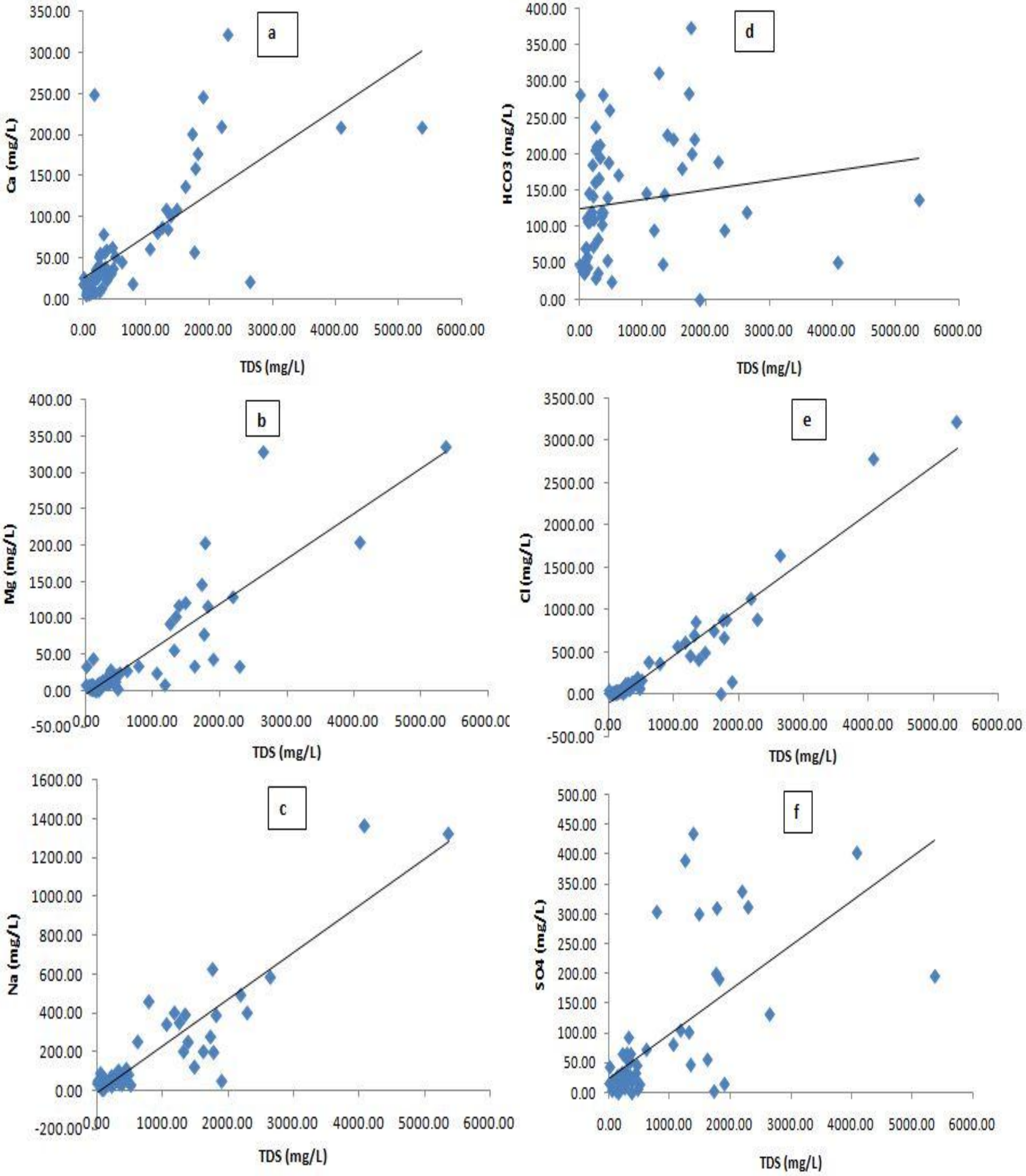

Fig 5.1: Scatter plots showing correlation between TDS and Ions.

5.1.3 Major Cation Chemistry

The concentration of Ca^{2+} ions in the study area ranges from 4.0 to 321.0 with an average of 24.4 mg/L while that of Mg^{2+} is from 0.9 to 335.0 with mean of 6.9 mg/L (Table 4.1). These indicate that Mg^{2+} concentration in the study area is relatively high as compared to Ca^{2+} concentration. The Ca^{2+}+Mg^{2+} vs. HCO_3^-+SO_4^{2-} scatter diagram (Fig. 4.4d) shows that majority of the samples fall above the equiline indicating that silicate weathering is the dominant process for supply of the magnesium and calcium ions to the groundwater (Bhat et al., 2013). 6 samples of Ca^{2+} and 4 samples of Mg^{2+} were beyond maximum permissible limit of 200 mg/L (WHO, 2011). Since HCO_3^- is the dominant anion in the groundwater of the study area, the elevated values recorded may be attributed to availability of the carbonate minerals in the recharge area (Elango et al. 2003). Therefore it can be concluded that dissolution of silicate mineral accounts for the excess levels of calcium and magnesium in the groundwater samples.

The concentration of Na^+ and K^+ ranges from 4.5 to 1366 mg/L and between 1.3 and 80.0 mg/L respectively (Table 4.1). From Fig. 4.4(a), it is possible that halite dissolution process (Na^+/Cl^- is approximately 1) is responsible for the Na^+ concentration in the ground water. In the area, 14 samples have Na^+ values above the WHO (2011) recommended limit of 200 mg/L. Among these are CC6, CC9, CC10, MF20, MF31 and AA62 with values 1325, 400, 1366, 250, 584 and 492 mg/L respectively among others. Potassium is relatively less common than sodium and its main source in groundwater in this study is weathering of potash silicate minerals, potash fertilizers and also due to surface water for irrigation (Ramesh and Jagadeeswari, 2012).

Also, the relationship between Na+K-Cl and Ca+Mg-HCO_3+SO_4 (Fig 4.5) shows that the hydrochemical behavior of the major ions in groundwater is due to cation exchange processes. The Na+K-Cl ions represent the contribution of a source that is dissolution of halite to the concentrations of Na^+ and K^+ in water, with K^+ coming from anthropogenic activities such as application of fertilizers. In other words, there is ion exchange of Na^+ and K^+ in water for Ca^{2+} and Mg^{2+} from rock (aquifer) (Bhat et al., 2013).

5.1.4 Major Anion Chemistry

Concentration of HCO_3^- in the study area extends from 0 to 373 mg/L with a mean value of 134 as shown in Table 4.1. Approximately 9.4% (6 samples) of the sampling stations have values exceeding the allowable limit of 240 mg/L set by the WHO (2011) guidelines for drinking water (Table 4.1). These samples consist of CC4, CC15, MF23, MF25, MF26 and AA51. A combination of HCO_3^-, with $CaCO_3$ and SO_4^{2-} forms heat retarding, pipe clogging scale in boilers and in other heat exchange equipment (Obiefuna and Sheriff, 2010). The HCO_3^- concentration in groundwater is derived from carbonate weathering (Jeevanandam et al. 2006; Kumar et al. 2009). In Fig 4.4c (Ca vs. HCO_3) majority of the samples plotted above the equiline which suggests that carbonate weathering as well as dissolution of carbonic acid in the aquifers in the area are the dominant processes responsible for the presence of HCO_3^-.

Chloride concentration in the groundwater samples ranged from 7.7 to 3216 mg/L and 18 samples (nearing 28.1%) are far above the WHO (2011) maximum allowable limits of 300 mg/L in drinking water (Table 4.1). Naturally, processes such as weathering, dissolution of salt deposits, and irrigation drainage return flow are responsible for chloride content in the groundwater (Lusczynski and Swarzenski 1996). Concentrations in excess of 250 mg/L are increasingly likely to be detected by taste, but some consumers may become accustomed to low levels of chloride-induced taste. High concentrations of Chloride (Cl^-) give a salty taste to water and beverages (WHO, 2011).

In this study, SO_4^{2-} has values ranging from 2.69 to 435 mg/L with 7 samples (representing 10.9%) which are above the 250 mg/L limit recommended by WHO (2011). SO_4^{2-} concentrations in the area are derived from weathering of sulfate and gypsum-bearing sedimentary rocks. Sulfate also occurs generally in urban runoff derived from the dissolution of street dust, rainwater runoff from buildings, and the dissolution of atmospheric dryfall, explains a substantial proportion of excess SO_4^{2-} ((Elango et al., 2003; Suh, 2004; Jeevanandam et al., 2006).

Concentrations of Fluoride in samples in area ranged from as low as 0 mg/L to as high as 3.39 mg/L (Table 4.1). The study area recorded 11 samples (representing 17.2%) which have values beyond the threshold of 1.5 mg/L. One of the essential components for maintaining normal and development of healthy teeth and bones is F^-. However, continuing consumption of higher concentrations, above 1.2 mg/l however cause dental flourosis (Rao, 2006) and in extreme cases even skeletal flourosis (Dissanayake, 1991), as in the cases of samples CC1 – CC4, MF25, AA32 and AA33 among others. The concentration of fluoride in groundwater is not uniform in the area, and the sources of these high values may be attributed to the difference in the presence and accessibility of fluorine-bearing minerals such fluorite to the circulating water and also due to leaching activities (www.ghanadistrict.com).

Trace metals are widely distributed in the environment with sources mainly from weathering of minerals and soils (Merian, 1991; O'Neil, 1993). The values of manganese found in the study are between 0 and 3.3 mg/L (Table 4.1) with as many as 39 samples representing about 60.9% found to be above the WHO (2011) allowable limit of 0.1 mg/L in potable water. Fe^{2+} concentration in the samples varies from 0 to 9.8 mg/L (Table 4.1). About 15.6% (10) of all the groundwater samples has elevated Fe^{2+} levels above WHO (2011) permissible limit of 1 mg/L for drinking. Trace metals are needed by the body to satisfy its nutritional needs. However, only small concentrations are required, as high doses can lead to health hazards (WHO, 2011). Trace metals are widely distributed in the environment with sources mainly from weathering of minerals and soils (Merian, 1991; O'Neil, 1993).

5.1.5 Mechanisms Controlling Groundwater Chemistry

Reactions between groundwater and aquifer minerals have a significant role on water quality, which are also useful to understand the genesis of groundwater (Cederstorm 1946; Gupta et al. 2008; Subramani et al. 2005). To know the groundwater chemistry and the relationship of the chemical components of water to their respective aquifers such as chemistry of the rock types, chemistry of precipitated water, and rate of evaporation, Gibbs (1970) put forward the ratio of cations and anions.

The Gibbs diagram (Fig. 4.6) indicates that majority of samples plot within the rock dominance category suggesting that the presence of ions in the groundwater system of the study area is from the geology (aquifer). A plot (Fig. 4.5) of alkali ions vs. alkaline earth ions illustrates a gradient that is approximately -1 (samples plotting close to the origin) indicating that cation exchange is a significant process controlling the chemistry of groundwater of the area, with much of the alkali ions being released from the chemical weathering and dissolution of halite (rock dominance).

5.1.6 Hydrogeochemical facies of groundwater

The values obtained from the physicochemical analysis of groundwater samples indicate that the dominant cation in the area is Na^+ and the anion is Cl^-, and the order of dominance ions is $Na^+ > Ca^{2+} > Mg^{2+} > K^+ : Cl^- > HCO_3^- > SO_4^{2-}$. It can be observed from Fig. 4.7 (Piper Diagram) that the general dominant water type of the study area is NaCl, and this suggests that throughout most of the study area alkali (Na^+ and K^+) dominate over alkaline earths (Ca^{2+} and Mg^{2+}) and strong acid (Cl^-) dominate over weak acids (HCO_3^-) in the groundwater. Samples obtained from CC and MF stations in the study area produced Na-Cl groundwater type (Figs. 4.8a and 4.8b), while those from AA stations gave rise to Na-Ca-Cl water type (Fig. 4.8c).

5.2 Quality Assessment of Groundwater for Irrigation Purpose

The quality of water, type of soil, and cropping practices play an important role for a suitable irrigation practice (Bhat et al., 2013). Presence of excessive amounts of dissolved ions in irrigation water affect plants and agricultural soil physically and chemically, thus reducing productivity. According Bhat et al. (2013), the physical effect of these ions is to lower the osmotic pressure in the plant structural cells, thus preventing water to reach the branches and leaves of the plant. The chemical effect is to disrupt plant metabolism.

In this work, the values of EC and SAR ranged from 2.6 to 9760 and 0 to 16.1 with an average value of 1288.63 μS/cm and 3.6 meq/L (Table 4.4) respectively. From, 31 samples fall into high (doubtful) (S3:18-26) and very high (unsuitable) (S4:>26) for irrigation purposes (Table 4.5). According to Yang et al. (2012), water of high sodium content and low calcium and magnesium concentrations can make the soil become compact and impervious. The salinity hazard classes based EC values of less than 250 and 250-750 μS/cm representing S1and S2 which are interpreted as low (excellent) and medium (good) for agriculture reasons respectively (Table 4.6). Fig. 4.7 is USSL diagram showing the relation between sodium and salinity hazard.

RSBC values of the study area are illustrated by Table 4.7 and Fig. 4.8. From Table 4.11, 3 samples are unsuitable for irrigation purposes. These samples are obtained from borehole stations CC4, MF25 and AA51. Higher cumulative concentration of HCO_3^- and CO_3^{2-} than Ca^{2+} and Mg^{2+} concentration is an indication that residual carbonate will react with sodium, thereby resulting into sodium hazard (Ishaku et al., 2012). Bicarbonate and carbonate is considered to be detrimental to the physical properties of soils, as it causes dissolution of organic matter in the soil, which in turn leaves a black stain on the soil surface on drying (Bhat et al., 2013). As a result, the relative proportion of sodium in the water is increased in the form of excess sodium carbonate. According to the US Department of Agriculture, water having more than 2.5 meq/L of RSC is not suitable for irrigation purposes, and that a high value of RSC in water leads to an increase in the adsorption of sodium in soil (Eaton 1950). Accordingly, 98.30% of samples fall in the suitable category and only 1.69% of the samples fall in the unsuitable category.

Percentage sodium is plotted against total ionic concentration in Fig. 4.11. It can be observed from diagram that 40 water samples (62.6%) are considered 'excellent to good', 2 and 8 samples representing 3.1 and 12.5% are 'good to permissible' and 'permissible to doubtful' respectively for irrigation purposes. If the concentration of Na^+ is high in irrigation water, Na^+ gets absorbed by clay particles, displacing Mg^{2+} and Ca^{2+} ions. This exchange process of Ca^{2+} and Mg^{2+} for Na^+ in the current study, water in the soil reduces the permeability of the soil and eventually results in poor internal drainage of the soil. Hence, air and water circulation is restricted during wet conditions and such soils are usually hard when dry (Collins and Jenkins 1996; Saleh et al. 1999).

Sodium measured against Ca^{2+} and Mg^{2+} was considered by Kelley (1963) for calculating KR using the formula (3.6) where, all the ions are expressed in meq/L. A look at Table 4.4 reveals that 10 samples nearing 25% fall outside the permissible limit of 1.0 meq/L and are considered unsuitable for irrigation purposes. The sample included in Table 4.7., indicates that most groundwater samples (75%) however, have KR within the permissible limit of 1.0 meq/L and are therefore considered suitable for irrigational practice. The increased presence of Ca^{2+} and Mg^{2+} in the groundwater is responsible for isolated cases of high values of KR in the study area.

An appraisal of Table 4.8 (classification of TDS of studied samples according to Robinove et al., (1958) reveals that, 46 samples are with values less than 1000 mg/L and are within the nonsaline category, and are therefore classified as excellent irrigation waters (Robinove et al., 1958). Sixteen and 2 samples indicating 25 and 3.1% respectively are said to be slightly and moderately saline. With this, salts from the major ions (Ca^{2+}, Na^{+}, Mg^{2+} and Cl^{-}) whose values are high in the study area can affect the osmotic activities of the plants. Because it was a secondary data, sample locations were not given GPS coordinate and therefore it was difficult to determine their positions with respect to the coast line and could not be possible to discuss the variations in concentration with respect to distance.

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATION

6.1 CONCLUSION

Hydrogeochemical data analyses and interpretation of groundwater samples for domestic purposes per WHO (2011) permissible limits shows that in study area, groundwater is generally acidic to alkaline in nature. Based on TDS, the groundwater in the study area falls under fresh (TDS<1000 mg/l) to brackish (TDS>1000 mg/l) types of water, as nearing 72% (46 samples) of groundwater is classified as fresh whilst 28% of samples is brackish water. TH values indicate that water samples exhibit characteristics of soft to very hard with 14 samples (21.9%) having hardness values beyond the maximum permissible limit of 500 mg/L for drinking water. From Figs. 5.1a, 5.1b and 5.1c, Ca^{2+}, Mg^{2+} and Na^{+} produce respectively 0.8, 0.9 and 0.8 correlation co-efficient (very strong relationship and linearity) with TDS suggesting the possibility of these ions resulting from the same process and source.

The scatter diagram (Fig. 4.4d) shows that majority of the samples fall above the equiline indicating that silicate weathering is the dominant process for supply of the magnesium and calcium ions to the groundwater. Six samples of Ca^{2+} and 4 samples of Mg^{2+} were beyond maximum permissible limit of 200 mg/L. The sum of Ca^{2+} concentration in the study area is relatively higher as compared to Mg^{2+}, Na^{+} and K^{+} concentrations. This therefore suggests that halite weathering is the dominant process responsible for the release of Na^{+}, Cl^{-} and SO_4^{2-} contents in the groundwater. Also, the relationship between Na+K-Cl and $Ca+Mg-HCO_3+SO_4$ (Fig. 4.5) shows that the hydrochemical behavior of the major ions in groundwater is due to cation exchange processes. The Na+K-Cl ions represent the contribution of a source that is dissolution of halite to the concentrations of Na^+ and K^+ in water. In other words, there is ion exchange of Na^+ and K^+ from rock (aquifer) for Ca^{2+} and Mg^{2+} in water.

In terms of anions, 7 samples (representing 10.9%) have values of SO_4^{2-} which are above the 250 mg/L recommended limit in drinking water. HCO_3^- on the other hand has approximately 9.4% (6 samples) of the sampling stations values exceeding the allowable limit of 240 mg/L set by the WHO (2011) guidelines for drinking water (Table 4.1). These samples consist of CC4, CC15, MF23, MF25, MF26 and AA51. Dissolution of halite, as illustrated by Fig 4.4a is responsible for the concentrations of Cl- and its excesses over 250 mg/L in the area. High concentrations of Chloride (Cl^-) give a salty taste to water and beverages.

The study area recorded 11 samples (representing 17.2%) which have values beyond the threshold of 1.5 mg/L (WHO standard). The continuing consumption of higher concentrations of F^- above 1.2mg/L can cause dental and skeletal flourosis as in the cases of samples CC1 – CC4, MF25, AA32 and AA33 among others.

Trace metals are widely distributed in the environment with sources mainly from weathering of minerals and soils. The range of values of manganese found in the study indicates 39 samples representing about 60.9% are above the recommended allowable limit of 0.1 mg/L in potable water. The source of iron in the study area can be adduced to dissolution of silicate, sulfides, and the presence of siderite and hydroxides. About 15.6% (10) of all the groundwater samples has elevated Fe^{2+} levels above permissible limit of 1 mg/L for drinking.

The values obtained from the physicochemical analysis of groundwater samples indicate that the dominant cation in the area is Na^{+} and the anion is Cl^{-}, and the order of dominance ions is $Na^{+}>Ca^{2+}>Mg^{2+}>K^{+}:Cl^{-}>HCO_3^{-}> SO_4^{2-}$. The Piper Diagram illustrates that the general dominant water type of the study area is NaCl. Throughout the study area, alkali (Na^{+} and K^{+}) dominate over alkaline earths (Ca^{2+} and Mg^{2+}) and strong acid (Cl^{-}) dominate over weak acids (HCO_3^{-}) in the groundwater.

In this work, the 31 samples fall into high (doubtful) (S3:18-26) and very high (unsuitable) (S4:>26) for irrigation purposes (Table 4.6). The salinity hazard classes based EC values of less than 250 and 250-750 µS/cm representing S1and S2 which are interpreted as low (excellent) and medium (good) for agriculture reasons respectively. RSBC values of the study depict that 3 samples are unsuitable for irrigation purposes. These samples are obtained from borehole stations CC4, MF25 and AA51.

Table 4.4 revealed that 10 samples nearing 25% fall outside the permissible limit of 1.0 meq/L based on KR, and are considered unsuitable for irrigation purposes. This indicates that most groundwater samples (75%) however, have KR within the permissible limit of 1.0 meq/L and are therefore considered suitable for irrigational practice. The increased presence of Na^{+}, Ca^{2+} and Mg^{2+} in the groundwater is responsible for isolated cases of high values of KR in the study area.

The nature of TDS in the water samples (Table 4.11) reveals that 46 samples are with values less than 1000 mg/L and are within the nonsaline category, and are therefore classified as excellent irrigation waters. Sixteen and 2 samples indicating 25 and 3.1% respectively are said to be slightly and moderately saline.

6.2 RECOMMENDATION

There is the need to educate the public on efficient water use methodologies and the intensification of the educational awareness as to how to handle and locally treat water for domestic use.

Farmers should be advised on the precautionary measures that need to be taken especially in CC station to forestall soil permeability and osmotic problems in plants, since most of the samples here have RSBC. Areas of inferior groundwater quality for irrigation should adopt appropriate soil amendments practices on agricultural farmlands.

District Assemblies to encourage communities to operate, manage and monitor units of trace metal levels in such boreholes with high levels of Fe^{2+} and Mn usually for early detection of aggravated levels for possible corrective measures to be taken to avoid hazards.

This work may serve as a preliminary study to provide baseline information that may direct future water quality assessment studies in the study area.

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APENDIX

Table A1. Physicochemical Parameters of the Study Area

Sample ID	pH	EC	TDS	Na	K	Ca	Mg	HCO_3	Cl	SO_4	NO_3	Fe	Mn	TH	TA	F
CC1	7.02	3050	1630	200	40.0	136	33.9	180.0	750	56	3.900	0.17	0.97	480	165.0	2.550
CC2	7.03	705	354	32.6	10.0	56.1	9.7	120.0	90	29	0.200	1.73	0.33	180	98.4	2.960
CC3	7.55	892	455	80.2	12.5	32.1	7.2	140.0	120	33	1.000	0.06	0.21	110	115.0	2.530
CC4	8.61	971	488	80.1	12.3	36.1	2.4	260.0	70.2	6	0.700	0.03	0.03	100	213.0	2.440
CC5	6.76	2640	1327	200	80.0	108	55.8	48.8	700	102	0.174	0.05		500	40.0	1.096
CC6	6.20	9760	5368	1325	32.8	208	335	137	3216	196	16.9	0.548	0.083	1900	112.0	<0.005
CC7	5.98	447	262	42.6	7.0	36.9	13.6	161	75.4	15.4	0.751	0.176	0.326	148	132.0	<0.005
CC8	6.47	556	306	84	8.6	33.7	10.7	83	132	33.5	6.09	0.046	0.19	128	68.0	0.546
CC9	6.20	2160	1188	400	4.3	80.2	8.4	95.2	615	105	1.88	0.161	0.424	235	78.0	0.51
CC10	6.43	74.3	4087	1366	10.8	208	204	51.2	2779	403	1.39	0.013	1.78	1360	42.0	<0.005
CC11	6.80	1945	1069	340	7.2	60.1	24.2	146	566	81.2	1.41	0.02	0.208	250	120.0	1.5
CC12	6.88	431	237	58	8.8	29.7	7.7	110	48.5	65.3	2.04	0.116	0.282	106	90.0	0.59
CC13	6.56	670	369	72	35.4	30.5	24.3	103	144	65.5	7.75	0.246	0.214	176	84.0	0.794
CC14	5.88	2540	1397	249	18.8	100	117	226	412	435	6	0.065	3.13	730	185.0	0.519
CC15	6.18	2300	1265	349	17.2	86.2	92.2	311	457	390	5.79	0.065	2.15	595	255.0	<0.005
MF16	6.88	3510	1786	196	68.2	158	203	200	670	310	<0.001	0.11		1100	164.0	1.262
MF17	7.25	2960	1494	120	40.8	108	121	220	495	300	0.111	0.07		770	180.0	0.915
MF18	6.73	192	90.7	12.4	3.8	9.6	5.8	36.6	25	18	<0.001	0.17		48	30.0	1.086
MF19	6.70	182	85.4	5.2	3.4	9.6	7.8	36.6	15	15	0.58	0.01		56	30.0	0.832
MF20	6.46	1140	627	250	10.4	44.1	27.6	171	383	72.6	2.42	3.74	1.5	224	140.0	0.537
MF21	11.70	3470	1909	47.5	4.4	245	43.4	0	149	15	7.55	0.064	<0.005	790	726.0	<0.005
MF22	6.40	610	336	100	8.4	32.9	14.1	195	87.4	54.4	0.58	1.54	0.37	140	160.0	0.102
MF23	6.45	3160	1738	276	24.4	200	146	283	7.66	2.69	7.25	0.053	1.11	1100	232.0	1.5
MF24	7.89	1781	797	458	7.8	17.6	34		367	304		0.196	0.066			
MF25	6.55	3220	1771	625	23.2	56.1	77.7	373	874	200	7.83	0.29	0.379	460	306.0	1.77
MF26	6.88	697	383	35.6	16.6	58.5	28.6	281	97.3	18.3	<0.001	0.102	0.054	264	230.0	0.04
MF27	2.26	3320	1826	387	26.6	176	116	220	885	191	<0.001	0.044	0.23	920	180.0	0.093
MF28	6.49	2460	1353	390	11.3	84.2	102	144	855	47.3	0.463	0.188	0.384	630	118.0	<0.005
MF29	6.86	862	473	79.2	11.0	61.7	21.8	188	169	46.1	<0.001	0.416	0.365	244	154.0	0.005
MF30	6.67	4180	2299	400	15.3	321	33.6	95.2	886	312	2.77	9.77	0.616	940	78.0	0.652
MF31	6.16	4820	2651	584	24.8	20	328	120	1641	132	3.15	0.245	<0.005	1400	98.0	1.47
AA32	6.13	487	232	20.9	11.8	24.1	3.8	73.2	14	26	23.4	0.08		76	60.0	3.39
AA33	6.35	287	135	22.4	9.8	6.4	1	58.7	10	9	6.4	0.16		20	48.1	3.33
AA34	6.15	346	190	37	8.0	248	9.2	112	47.6	20.4	20.5	2.06	0.344	100	92.0	1.27
AA35	6.94	427	203	34	10.8	25.7	0.9	120.0	35	20.0	<0.001	1.8		68	98.4	3.130
AA36	6.50	131	61.5	87	3.8	4.01	7.3	39	15	4	0.9	0.91		16	32.0	2.63
AA37	6.69	237	130	57	7.7	12	6.8	112	42.8	3.7	0.516	4.62	0.216	58	92.0	0.883
AA38	6.16	222	122	28.5	2.3	8	44	70.8	25.8	13.9	3.66	0.192	0.415	38	58.0	0.626
AA39	6.94	427	203	34	10.8	7	0.9	120	35	20	<0.001	1.8		68	98.4	3.13
AA40	6.31	481	265	40.2	7.8	50.5	12.6	205	59.6	33.1	0.313	0.036	0.279	178	168.0	0.759
AA41	6.60	485	267	37	7.0	40.9	14	237	36.7	14.1	3.13	0.181	0.494	160	194.0	1.5

Table A1 (Contd)

AA42	5.22	258	142	28.3	7.3	12	2.4	43.9	27.8	26.9	11.1	0.04	0.014	40	36.0	0.528
AA43	5.70	947	521	27	8.9	50.5	24.7	24.4	168	14.4	4.65	0.037	0.1	228	20.0	0.35
AA44	6.27	580	319	55	6.2	32.1	16.5	166	63.5	55	0.422	0.027		148	136.0	<0.005
AA45	6.75	609	335	62.5	9.5	77.8	11.1	212	62.5	92.9	1.64	1.37	0.396	240	174.0	0.253
AA46	5.60	2.6	146	34.2	4.9	20.8	3.9	107	35.7	11	2.61	0.596	0.096	68	88.0	0.235
AA47	5.61	559	307	85	22.2	12	13.1	36.6	118	65.9	5.25	<0.01	0.306	84	30.0	2.2
AA48	6.11	513	282	51.5	6.8	54.5	9.7	210	55.6	27.4	0.921	0.3	0.259	176	172.0	<0.005
AA49	5.75	663	365	52.7	8.6	37.7	16.5	115	97.3	52.9	4.48	<0.01	0.122	162	94.0	1.25
AA50	4.83	190	105	38.7	2.7	4.8	1.5	53.7	33.7	6.87	3.82	<0.01	0.124	18	44.0	<0.005
AA51	7.35	447	24.6	48	5.3	24.8	33.5	281	14.9	43.4	0.356	0.188	0.401	200	230.0	0.67
AA52	6.53	327	18	35	3.6	16.8	7.8	47.6	49.6	15.8	0.603	0.014	<0.005	74	8.0	<0.005
AA53	5.84	157	86.4	16.8	3.4	8	3.9	46.6	18.9	12	7.43	0.01	0.064	36	38.0	<0.005
AA54	5.78	190.3	105	24.9	4.9	13.6	3.9		22.8	18.2		0.088	0.113			
AA55	6.44	414	228	72	4.7	36.1	6.8	142	80.5	33.8	0.964	0.669	0.231	118	116.0	0.998
AA56	6.85	396	218	55	6.9	34.5	10.7	185	50.8	25.4	0.857	0.146	0.44	130	152.0	0.626
AA57	6.30	302	166	27	8.9	24.8	9,7	146	25.8	<0.001	5.14	<0.01	0.281	102	120.0	1.02
AA58	5.70	823	453	110	7.8	29.7	13.1	53.7	199	21.2	4.29	0.027	0.188	128	44.0	0.759
AA59	5.84	126	69.3	15	3.6	7.2	2.9	39	10.9	20.4	4.25	<0.01	0.01	30	32.0	<0.005
AA60	5.99	309	169	42.6	4.4	20	5.3	107	41.7	28.8	4.16	3.55	0.347	72	88.0	0.182
AA61	7.21	232	109	4.5	1.3	19.2	8.7	70.4	15	15	<0.001	0.15		84	57.7	0.697
AA62	6.04	4000	2200	492	2.7	209	129	189	1132	338	<0.001	0.023	0.269	1050	155.0	<0.005
AA63	6.56	701	386	30	80.0	21.6	22.3	120	146	<0.001	0.953	0.169	0.218	146	98.0	0.732
AA64	5.33	491	270	61	19.7	8	11.2	29.3	123	7.98	<0.001	0.621	0.779	66	24.0	<0.05

Table A2: Parameters used for the evaluation of Groundwater Quality for Irrigation Purpose

Station	SAR	RSBC	KR	%Na	EC	TDS	TH
CC1	3.96	-3.85	0.90	50.26	3050	1630	480
CC2	1.06	-0.84	0.39	31.70	705	354	180
CC3	3.32	0.69	1.58	63.29	892	455	110
CC4	3.47	2.65	1.73	65.40	971	488	100
CC5	3.88	-4.60	0.87	51.68	2640	1327	500
CC6	13.16	-8.15	1.50	60.40	9760	5368	1900
CC7	1.52	0.79	0.62	40.52	447	262	148
CC8	3.21	-0.33	1.41	60.00	556	306	128
CC9	11.33	-2.45	3.69	78.79	2160	1188	235
CC10	16.05	-9.56	2.17	68.53	74.3	4087	1360
CC11	9.32	-0.62	2.94	74.84	1945	1069	250
CC12	2.44	0.31	1.18	56.35	431	237	106
CC13	2.35	0.16	0.88	53.16	670	369	176
CC14	3.99	-1.30	0.73	43.40	2540	1397	730
CC15	6.20	0.79	1.27	56.56	2300	1265	595
MF16	2.42	-4.62	0.34	29.27	3510	1786	1100
MF17	1.88	-1.79	0.34	28.83	2960	1494	770
MF18	0.78	0.12	0.56	40.00	192	90.7	48
MF19	0.31	0.12	0.20	22.07	182	85.4	56
MF20	7.24	0.59	2.41	71.18	1140	627	224
MF21	0.73	-12.25	0.13	12.08	3470	1909	790
MF22	3.66	1.55	1.54	61.76	610	336	140
MF23	3.60	-5.36	0.54	36.29	3160	1738	1100
MF24	14.62	-0.88	5.37	84.42	1781	797	0.0
MF25	12.61	3.30	2.92	74.93	3220	1771	460
MF26	0.95	1.68	0.29	27.16	697	383	264
MF27	5.54	-5.19	0.91	48.67	3320	1826	920
MF28	6.73	-1.85	1.33	57.58	2460	1353	630
MF29	2.20	-0.01	0.70	43.11	862	473	244
MF30	5.66	-14.49	0.92	48.54	4180	2299	940
MF31	6.75	0.97	0.90	47.88	4820	2651	1400
AA32	1.04	-0.01	0.59	44.16	487	232	76
AA33	2.17	0.64	2.43	75.31	287	135	20
AA34	0.63	-10.56	0.12	12.14	346	190	100
AA35	1.79	0.68	1.08	56.23	427	203	68
AA36	5.94	0.44	4.67	82.73	131	61.5	16
AA37	3.24	1.24	2.12	69.61	237	130	58
AA38	0.87	0.76	0.30	24.21	222	122	38
AA39	3.19	1.62	3.44	80.37	427	203	68
AA40	1.31	0.83	0.49	35.26	481	265	178
AA41	1.27	1.84	0.50	35.73	485	267	160
AA42	1.94	0.12	1.54	63.96	258	142	40

Table A2 (Contd.)

AA43	0.77	-2.13	0.25	23.37	947	521	228
AA44	1.95	1.11	0.80	46.03	580	319	148
AA45	1.75	-0.41	0.56	38.05	609	335	240
AA46	1.80	0.71	1.09	54.18	2.6	146	68
AA47	4.03	0.00	2.19	71.64	559	307	84
AA48	1.68	0.71	0.63	40.50	513	282	176
AA49	1.79	0.00	0.70	43.43	663	365	162
AA50	3.91	0.64	4.54	82.55	190	105	18
AA51	1.47	3.37	0.52	35.62	447	24.6	200
AA52	1.76	-0.06	1.02	51.94	327	18	74
AA53	1.21	0.36	1.00	52.90	157	86.4	36
AA54	1.52	-0.68	1.07	54.50	190.3	105	0.0
AA55	2.87	0.52	1.32	57.73	414	228	118
AA56	2.09	1.30	0.91	49.52	396	218	130
AA57	0.0	1.15	0.0	0.00	302	166	102
AA58	4.21	-0.61	1.85	65.87	823	453	128
AA59	1.19	0.28	1.08	55.22	126	69.3	30
AA60	2.18	0.75	1.28	57.65	309	169	72
AA61	0.22	0.19	0.12	11.98	232	109	84
AA62	6.57	-7.35	1.01	50.30	4000	2200	1050
AA63	1.07	0.89	0.44	53.26	701	386	146
AA64	3.25	0.08	1.99	70.38	491	270	66