UNIVERSITY FOR DEVELOPMENT STUDIES

GROUNDWATER RECHARGE AND HYDROCHEMICAL STUDIESATATANKWIDI CATCHMENT

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BY

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[DISSERTATION SUBMITTED TO THE DEPARTMENT OF APPLIED CHEMISTRY AND BIOCHEMISTRY, FACULTY OF APPLIED SCIENCES, UNIVERSITY FOR DEVELOPMENT STUDIES IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF MASTER OF PHILOSOPHY APPLIED CHEMISTRY]

DECEMBER,2016

DECLARATION

Student

I hereby declare that this thesis is the result of my own original work and that no part of it has been presented for another degree in this University or elsewhere:

Candidate’s Signature:…………………………. Date:…………………………

SUPERVISORS'S

I hereby declare that the preparation and presentation of this thesis was supervised in accordance with the guidelines on supervision of thesis laid down by the University for Development Studies.

Principal Supervisor's Signature:………………………… Date:……………………...

Name: Dr. K. B. Pelig-Ba (Ph.D)

Co-Supervisor's Signature:………………………………. Date:……………………

Name: Professor F. Addo-Yobo

ABSTRACT

The rate of groundwater recharge and the processes that affect groundwater quality at the Atankwidi Catchment were investigated in this study. The rate of recharge was estimated using Water Balance Method (WBM) and Chloride Mass Balance (CMB) method and compared. The rate of recharge by the WBM was 6% whiles point recharge by CMB method averaged 5.7% and ranged from 1.6 to 16% of mean annual rainfall. Hydrochemical analysis of groundwater showed varied concentrations of cations and anions in the order $Na^{+} > Ca^{2+} > Mg^{2+} > K^{+}$ and $HCO_3^{-} > Cl^{-} > SO_4^{2-} > NO_3^{-}$ respectively. Geochemical assessment of major ions using bi-plots suggested that, the occurrence of these ions in groundwater were controlled by mainly dissolution of silicate minerals and ion exchange reactions. This was supported by principal component analysis (PCA) of major ions and Gibbs diagram which suggested that the groundwater quality in the Atankwidi Catchment was mainly controlled by rock water interactions and to some lesser extent anthropogenic activities probably through application of both organic and inorganic fertilisers. Hierarchical cluster analysis of the major ions classified the groundwater into three groups. The groups showed different degree of rock water interactions. The major distinguishing factor among the groups was the total dissolved solids which generally increased from group one to group three. Piper diagram also classified the groundwater into three main hydrochemicalfacies in the order of $Na\text{-}Ca\text{-}HCO_3$, $Na\text{-}Ca\text{-}Mg\text{-}HCO_3$ and $Na\text{-}HCO_3$. The occurrence of these hydrochemicalfacies supported the PCA and Gibbs diagram. The concentrations of elements such as As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Zn and Pb were generally within the WHO guidelines for drinking-water. Groundwater quality was also found to be suitable for drinking based on the water quality index. The assessment of groundwater quality based on salinity index, United States Salinity

Laboratory (USSL) diagram, sodium percentage and Wilcox diagram showed that groundwater from the Atankwidi Catchment was suitable for irrigation on wide range of soils. However, problems associated with magnesium hazard and residual sodium carbonate is likely to limit its use.

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DEDICATION

In loving memory of my brother, Godwin Agyekum.

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CHAPTER ONE

INTRODUCTION

1.1 Background

Fresh water is essential to the existence of man and all living things. It is a very important natural resource which forms the core of the ecological system (WHO/UNICEF, 2014). The availability of freshwater resources plays a key role in promoting good living standards, enhancing economic growth, food security and livelihood, and eventually alleviating poverty(Adomako, 2010).

Many rural communities in Ghana have traditionally relied on surface water from streams, rivers, lakes, ponds, dugouts and impoundment reservoirs as their source of water supply for domestic uses (Gyau-Boakye and Dapaa-Siakwan, 2000). Most of such water sources are often polluted and have serious health implications as far as water-borne and water-related diseases like diarrhoea, cholera, guinea worm, bilharzia and others are concerned (WARM, 1998; Gyau-Boakye and Dapaa-Siakwan, 2000). The recurrence of these water-related diseases has made groundwater preferred choice over surface water as a source of portable water supply particularly in rural communities such as those in the Atankwidi Catchment area(Gyau-Boakye and Dapaa-Siakwan, 2000). In Ghana, it has been reported that about 62 to 71% of the rural and suburban water comes from groundwater (GEMS/Water Project, 1997). This makes groundwater a very important natural resource in Ghana.

Groundwater is increasingly become an alternate source of water supply for domestic, irrigation and industrial useprobably because it is generally of accepted quality and requires less or no chemical treatment prior to use, it iseasy and less expensive to develop closer to sources where it is needed(Macdonald and Davies, 2000).

Groundwater provide water security for drought prone areas (Gyau-Boakye and Dapaa-Siakwan, 2000; Siebert *et al*., 2010) such as Northern Ghana where Atankwidi catchment is located.

Groundwater is a major source of water supply for mainly domesticactivities in northern part of Ghana. This is perhaps due to the dispersed nature of the settlements. Also, the northern part of Ghana is characterised by prolonged drought. Rainfall decreases the further north one travels. This coupled with short rainfall season and prolonged drought makes communities to often experience inadequate surface water benefits and therefore depend on groundwater.

The major surface water sources in the Atankwidi Catchment area includes tributaries and sub-tributaries of the White Volta River and few traditional dams all of which but a few dams get dried up during the dry season. Besides that the non-ephemeral dams areoften heavily polluted. Communities within the Catchment area therefore depend largely on groundwater for mainly domestic purposes. The main occupation for majority of the people is rain-fed farming alongside small scale animal rearing with a few into petty trading and traditional cloth weaving. However, a few farmers also practice traditional irrigation along river banks from dug-out wells.Groundwater development in the basin therefore contributes enormously to the socio-economic status of the people living in the sub-basin. As a result, its assessment estimation, sustainability and proper management is a major concern. The thrust by the communities in the Atankwidi catchment to use groundwater for their domestic and agricultural activities is high but the groundwater recharge and the hydrochemical processes that control its qualityand the vulnerability of the aquifer to pollution are unknown. It is on this basis that this work seeks to evaluate the groundwater recharge and the hydrochemical process that control the groundwater quality at the Atankwidi Catchment area.

1.2 Problem Statement

Many communities in the Upper East region depend largely on groundwater as a source of water supply for domestic purposes (Martin, 2006). On the average, about 70% of the population of Upper East region depend largely on groundwater as a source of portable water and in the dry season, fairly used for irrigation purposes (Adetunde and Glover, 2010; Ofosu et al., 2010; Ofosu, 2011; Oyelude et al., 2013). Barnie *et al*., (2014) reported that groundwater increasingly become a source of water supply for small scale traditional irrigation. It has also been reported that, the Atankwidi catchment is among the sub-basins in the White Volta River Basin with high groundwater use per square kilometre (Martin, 2006). Obuobie, (2014) reported that total groundwater abstraction in the Catchment area as at 2010 stood at 549,000 m^3 for a population of 45,841.

In spite of the high dependence on groundwater in the Atankwidi Catchment area, there is little understanding about the rate which the aquifer is recharged. In addition to that, thehydrochemical processes that control the groundwater quality in the area are unknown. The continuous dependence on groundwater in the study area without proper understanding of the rate at which the aquifer is replenished could affect not only its quantity but the quality also. Gyau-Boakye and Dapaa-Siakwan (2000) observed groundwater decline in the semi-arid northern part of Ghana and some areas in the south due to excessive reliance on groundwater resources. Fetter (1994) reported that groundwater can be mined in similar manner as minerals, whenever groundwater is withdrawn at a rate greater than the rate of recharge to the aquifer.Also the use of water in general and not limited to groundwater for a particular purpose is determined by its quality which intend is controlled by the diversehydrogeochemical processes that takes place within the aquifer as well as anthropogenic activities.

The main occupation of the people in the area is rain-fed farming alongside small scale dry season traditional irrigation along river banks. The main cultivated crops include maize, millet, sorghum, rice and groundnuts during the raining season and mainly tomatoes and pepper during the dry season. Fetilisers are usually applied to maize, rice and vegetables to boost productivity (Laary, 2012). Anthropogenic activities such as agricultural practices through the application of agrochemicals particularly fertilizers can pose a serious threat to the groundwater (British Geological Survey, 2009).

Furthermore, the study area is in a crystalline rock terrain where the occurrence of groundwater is mainly controlled by secondary porosity as a result of chemical weathering, faulting and fracturing (SNC-Lavalin/INRS, 2011). Thus, wells and borehole sited are in fractured or sheared zone. Therefore, the probability of easy gravitational movement of water into aquifer is high (Akiti, 1982). Again, the main aquifer in the study area is the regolith aquifer in the weathered zone and the depth of the water table range from 5 to 30 m (Martin, 2006). This makes the aquifer more susceptible to environmental influences which could affect the groundwater quantity and quality.

Major studies on groundwater in Atankwidi Catchment focuses on the effect of climate change on small scale farmers, sustainable small scale irrigationdevelopment and its socio-economic importance(Martin, 2006; Laube and Le, 2007; Van den Berg, 2008; Barry *et al*., 2010; Namara *et al*., 2011; Obuobie, 2014).Therefore, groundwater recharge and hydrochemical studies in the study area are required for the proper and efficient management of groundwater resources in the area.

1.3 Objectives of the Study

The aim of this work is to assess groundwater recharge and investigate the hydrochemical processes that control the groundwater quality in the Atankwidi Catchment. To achieve this, the following objectives were set:

i. Quantitatively estimate the groundwater recharge using two methods; Water Balance Method (WBM) and the Chloride Mass Balance (CMB) method and compare the results.

ii. Assess the chemical quality of groundwater in the study area.

iii. Assess the suitability of groundwater in the Atankwidi Catchment for domestic and irrigation purposes from the perspective of hydrochemistry.

1.4 Justification

The rate of recharge to groundwater is an important tool for the sustainable management of groundwater resources. The sustainability of an aquifer depends on the amount of water that reaches the groundwater reservoir as recharge and the amount that is drawn from it over a period of time.The rate of natural recharge to aquifers is a prerequisite for efficient and sustainable management of groundwater resources (Marei *et al.*, 2010) and very crucial for assessinggroundwater quantity and quality(Afrifa, 2013).Communities within the Atankwidi catchment area mostly depend on groundwater for domestic and agricultural purposes.A good estimate of the rate of recharge to the aquifer is therefore essential for the proper management of the aquifer to prevent significant decline in the water table in the area.Estimation of groundwater recharge within an area would also help to identify recharge and discharge areasfor good measures to be taken to protect such zones from contamination (Afrifa, 2013).

Also, knowing the quality of groundwater is as important as its quantity because it determines its intended use. The use of water for domestic, irrigation or industrial purpose is to much extent determined by its quality(Hem, 1985). Furthermore, understanding of the various processes that control the quantity and quality of groundwater resources, their interaction with the surface environment and subsurface geology as well as the potential impacts of using these resources for water supply is crucial for sustainable management of groundwater resources (Afrifa, 2013).

1.4 Structure of Thesis

The thesis is divided into six chapters.**Chapter one** deals withthe problems of groundwater recharge and quality assessment in the Atankwidi Catchment. It also outlines the aim and objectives of this study. **Chapter two** describes the study area in realation to loction, climate and vegetation. Brief accounts ongeology and hydrogeology is also presented under this chapter. Review of relevant literatureis presented in**Chapter three**. It further explains the concepts of groundwater recharge and discusses groundwater quality assessment elsewhere and their relevance to the current study. **Chapter four** explains methods employed.Results and interpretations are presented in **Chapter five**. It also discusses the major findings. **Chapter six** contain conclusion and recommendations.

CHAPTER TWO

LOCATION, PHYSIOGRAPHICALAND GEOLOGICALSETTINGS OF THE STUDY AREA

2.1 Location of the Catchment Area

The Atankwidi Basin(Figure .) is located in the Upper East Region of Ghana. It is a sub-basin of the White Volta River and covers an area of about 286 km^2(Barry *et al.*, 2010).The catchment area extends to parts of Burkina Faso and parts ofnorthern Ghana. However, this study was based on the catchment area within Ghana to avoid cross boundary problems.

2.2.Climate and Vegetation

The area falls within the semi-arid Sudan-Savanna vegetation zone, with sparsely distributed trees like the baobab, shea nut, neem, and acacia naturally surrounded by grasses and shrubs (Martin, 2006; Barry *et al.*, 2010). The rainfall parttern is mono-modal, which begins from May and ends in October. The long term mean annual rainfall is 997 mm calculated from rainfall data from 1961 to 2012(Ghana Meteorological Agency (GMA), 2015). Temperatures are usually high with an average of 28.6 ℃. The mean daily minimum temperature is about 25℃, coinciding with the peak of the rainy season and rises to a maximum of 34℃ in April. However, monthly averages range from 26.4 °C at the peak of the rainy season in August to a maximum of 32.1°C in April (Kranjac-Berisaljevic *et al.*, 1998). The total evapotranspiration of 2050 mm exceeds the annual rainfall more than twofolds. High relative humidity of 65% is observed during the rainy season and decrease rapidly at the end of the rainy season toabout 10% during the harmattan period between December and January (Martin, 2006).

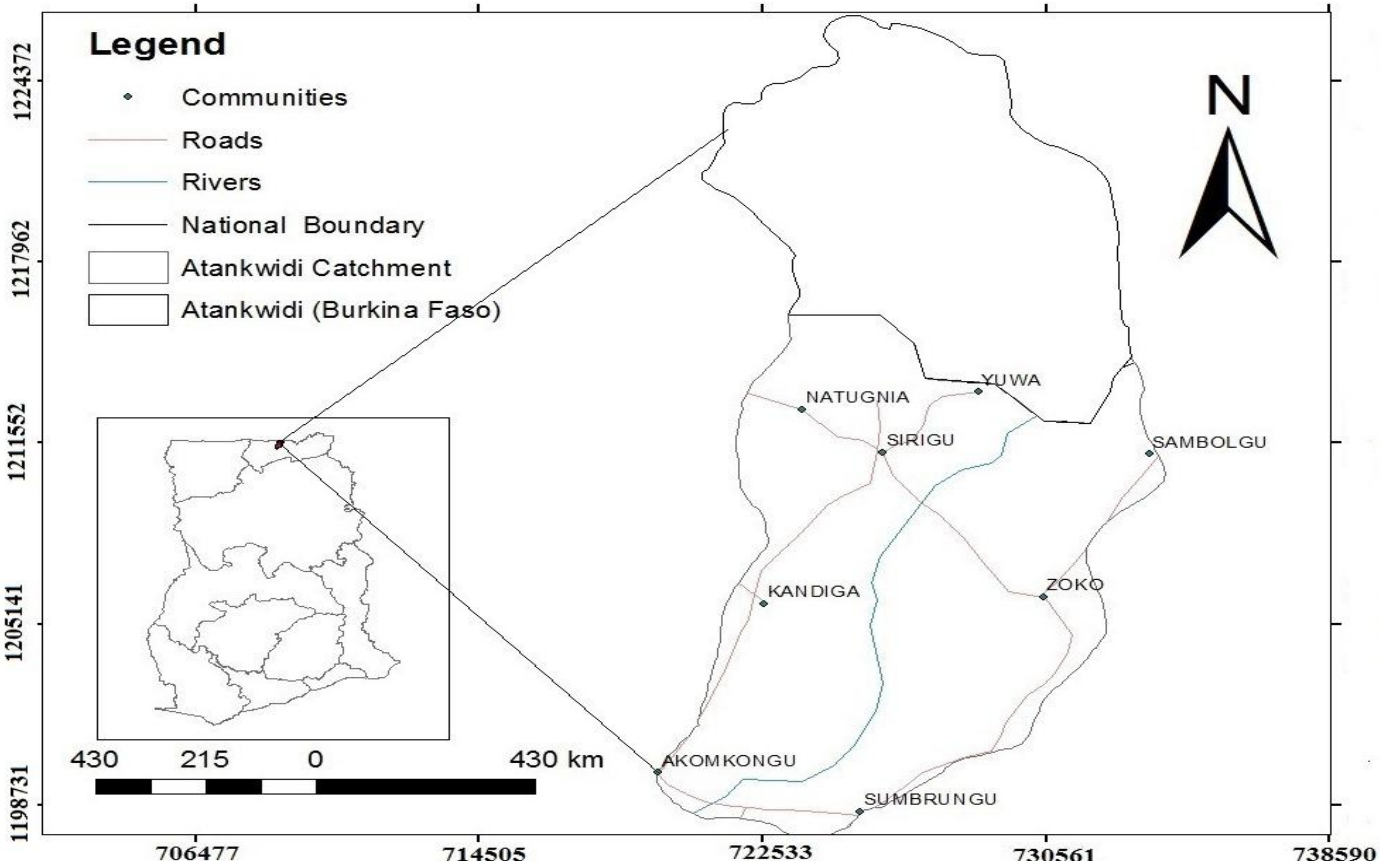


Figure .: Location map of Atankwidi Basin showing major communities

2.3 Geology of the study area

The study area forms part of Bole-Navrongo-NangodiBirimian Greenstone Belt of Ghana and trends generally southwest-northeast but there are some local N-S striking rocks at some areas (Kesse, 1985 Figure 2.3). Underlying the area are metamorphosed lavas and pyroclastic suite of rocks intruded at places by migmatite bodies and granodiorites(Leube *et al*., 1990). According to Milési *et al*., (1989) three types of granitoids in terms of mineralogical compositions are found in the area which belong to the *Belt* and *Basin* granites. These are mica–rich intrusive varieties which tend to border the volcanic belt and consist of:

(1) Coarse grained porphyrogranites generally consisting of hornblende, biotite-bearing granitoids and granodiorites with associated quartz veins and dolerite dykes and

(2) Coarse to medium grained microcline–rich granites, foliated and locally referred to as Bongo granites. These igneous intrusive occurs within the metasedimentary package and cover most parts of the area. There are also three hornblende-rich varieties that are closely associated with the metavolcanic rocks and known as the 'Dixcove' or 'belt' type.

2.4 Hydrogeology

TheAtankwidi Sub-basin is underlainedthe Precambrian Basement (PCB) rocks (SNC-Lavalin/INRS, 2011). Rocks of the PCB has been reported have low primary porosities and permeabilities. Hence groundwater occurrence and flow in such basement rocks are mainly controlled by secondary porosity as a result of weathering, faulting and fracturing(SNC-Lavalin/INRS, 2011).The characteristics of aquifers in such environments are reportedly variable, primarily due to anisotropic nature of

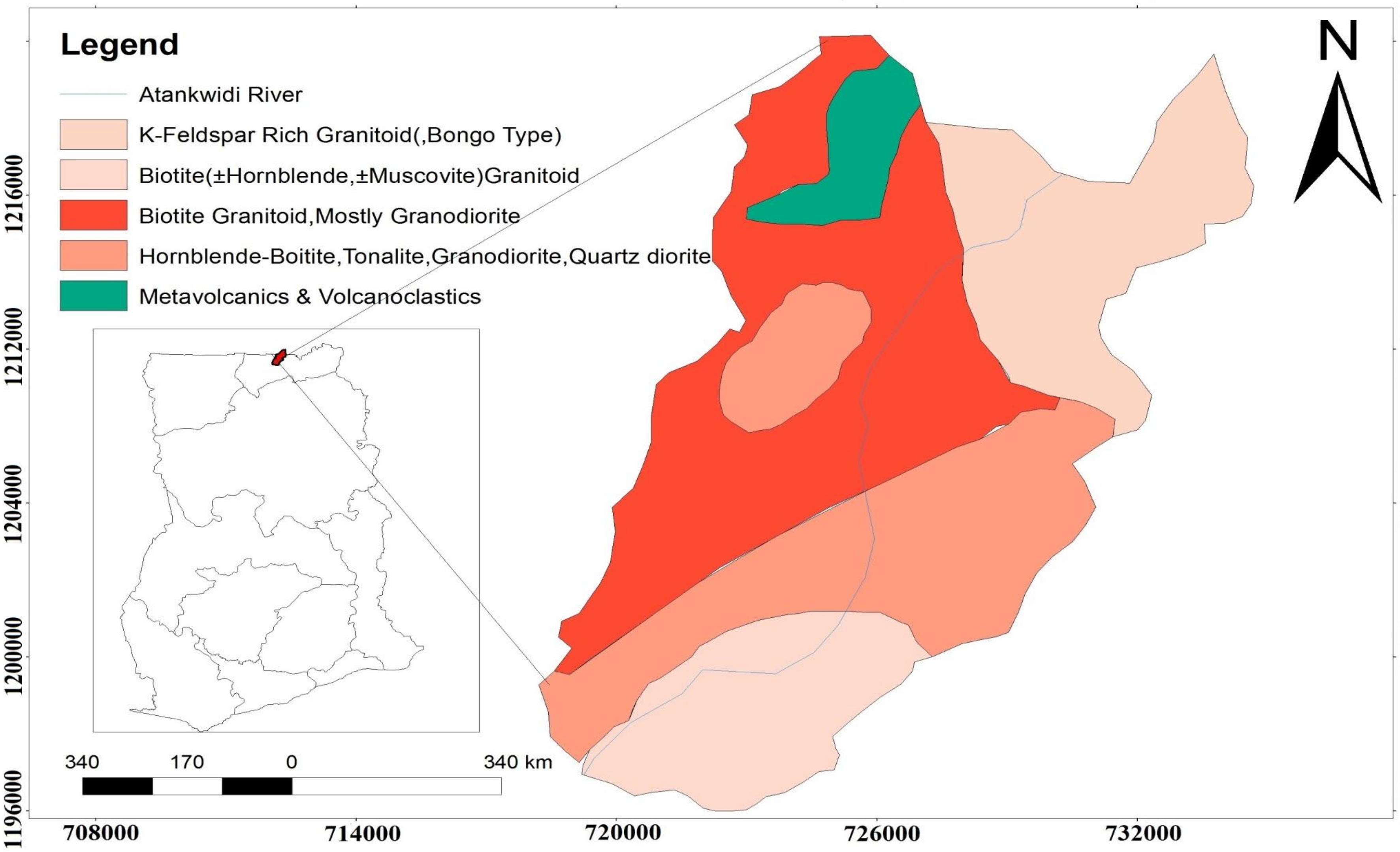


Figure .: Map showing the geology of Atankwidi

fracture networks, the complexity and variable intensity of weathering processes involved in regolith development (SNC-Lavalin/INRS, 2011).

Groundwater generally occurs the lower part of the saprolite and the upper part of the fractured bedrock (saprock), which generally complements each other in terms of permeability and storage. The upper, less permeable, part of the saprolite can act as a confining or semi-confining layer for this productive zone while the lower, usually saturated part of the saprolite is characterized by lower secondary clay content as groundwater flow can remove dissolved minerals, thus creating a zone of enhanced hydraulic conductivity. Nathan and Harris (1970) reported that on the average, areas underlain by rocks of the Birimian System (PCB rocks) exhibit deeper weathering of about 23 m and weathering has been known to have a significant impact on water storage capacity in crystalline rocks (Larsson, 1984). It has also been reported that, important subvertical fracture or fault zones originating from tectonic activity can be present at great depths (>150 m) and provide significant amounts of groundwater (SNC-Lavalin/INRS, 2011). Generally, borehole depth in the PCB rocks is averagely reported to be less than 80 m(Agyekum, 2004).

The hydrogeology of the study area consists of three aquifers (Martin, 2006; Van den Berg, 2008). These are discontinuous shallow aquifer, regolith aquifer and the fractured aquifer. The thickness of the shallow aquifer is about 1 m covering a less permeable clay material. This shallow aquifer dries up in the dry season and is the main source of water supply for traditional hand dug wells(Martin, 2006). The regolithaquifer is composed of an *in situ* of chemically weathered rock materials (regolith) underlain by the unweathered bedrock and it is the main aquifer in the study area. About 80% of all boreholes target the weathered rock aquifer (Martin, 2006).

Atypical weathering profile consist of highly decomposed rock materials rich in clay near the surface and becomes slightly weathered with decreasing clay content with depth until fresh rock is encountered(Chilton and Foster, 1995). The regolith aquifer has an average saturated thickness of 25 m and a hydraulic conductivity of 2.5 x 10^{-6} to 2.5 x 10^{-5} m/s (Martin, 2006) and low resistivity ranging from 3.2-55.3 ohm-m (Barry *et al.*, 2010). The depth of the water table in the study area range from 5 to 35 m (Martin, 2006).

2.5 Land-use Activities

The population of the study area is estimated at 45,841 (Ghana Statistical Service, 2012). The major type of work for majority of the population is rain-fed farming alongside small scale animal rearing with a few into petty trading and traditional cloth weaving. The main types of crops cultivated include millet, groundnut, rice, sorghum, cowpea, and maize on a small scale. Only a small fraction of the farmers practice traditional irrigation farming along river banks on small scale during the dry season. The main irrigated crops are tomatoes and pepper. A field survey revealed that farmers apply both organic and inorganic fertilserson their farms. The major use of groundwater in Atankwidi catchment is largely for domestic purposes and irrigation to a lesser extent. Other uses of water in the catchment area are for watering farm animals and building houses.

CHAPTER THREE

LITERATURE REVIEW

3.1Groundwater Recharge

Groundwater recharge is the percolation of water into the saturated zone forming an addition to the water table, together with the associated flow away from the water table within the saturated zone(Freeze and Cherry, 1979). It is process through which groundwater is replenished. Lerner *et al*., (1990) however, conceptually defined the principal recharge mechanisms from these sources as: (i) direct recharge; water added to the groundwater reservoir in excess of soil-moisture deficits and evapotranspiration by direct vertical percolation through the vadose zone, (ii) indirect recharge as; percolation to the water table through the beds of surface-water courses and (iii) localized recharge; an intermediate form of groundwater recharge resulting from the horizontal (near-) surface concentration of water in the absence of well-defined channels.

3.1.1Groundwater Recharge Studies

Different methods have been formulated for the estimation of groundwater recharge. These include tracer techniques, hydrologic budget techniques, the Darcy methods and numerical modeling(Lerner *et al.*, 1990; Kinzelbach *et al*., 2002; Scanlon *et al.*, 2002; de Silva and Rushton, 2007). Detailed reviews of different methods for the estimation of groundwater recharge have been provided by (de Vries and Simmers, 2002; Scanlon and Cook, 2002; Kinzelbach *et al*., 2002; Scanlon *et al*., 2002, 2006).

Different methods such as the water balance including baseflow, (Farquharson and Bullock, 1992; Pelig-Ba, 2004; Martin, 2006) and chloride mass balancemethod

(Edmunds *et al.*, 1988; Beekman and Sunguro, 2002; Adomako, 2010; Afrifa, 2013) have been used to estimate groundwater recharge in arid and semi-arid regions of Africa underlain by metamorphic or igeneous rocks (crystalline basement rocks). None of these methods though, separately gives a satisfactory result due to the heterogeneity and discontinuity of the aquifer and the complex nature of the resultant flow system(Chilton and Foster, 1995). However recharge rates of 0-25% of annual rainfall are often quoted in these aquifers (Nyagwambo, 2006).

Allen and Davidson (1982)used the ratio of chloride in rainfall and groundwater (Chloride mass balance method) and obtained recharge of 0.05-0.5% in Western Australia where the geological formation consist of granitic and volcanic fractured rocks however, the potential evapotranspiration exceeded precipitation by about three to 10 times. Groundwater recharge in crystalline rocks can be influenced by (i) the mode of chemical weathering and surface runoff and (ii) the intensity of the fracturing(Lerner, 1997).

Sukhija and Rao (1983) used environmental tritium and radioactive carbon studies to assess the groundwater recharge in granitic terrain ofVedavati River Basin, India andobtained recharge of 13-23% and suggested that in granitic terrain the recharge is dependent on the annual rainfall as well as the potential evapotranspiration.

Cook *et al.*, (1989) used chloride profiles and electromagnetic techniques to estimate groundwater recharge in semiarid region of Southern Australia. They obtained recharge rate of 0 – 25% and also observed that, recharge appeared to be approximately log-normally distributed with infiltration rate and hydraulic conductivity.

Ting, *et al*., (1998) reported recharge of 15% in Pingtung Plain in Taiwan using the chloride mass balance. This excluded recharge from additional irrigation water. Using chloride mass-balance method in the West Bank, Palestine, Marei *et al*., (2010) reported recharge rates between 5 and 50% of annual precipitation and observed that the geology and the climate conditions of the western slope had significant impact on the rate of recharge.

Tyner *et al*., (1999) used chloride mass balance and estimated groundwater recharge rates ranging from 12.2 to 38.9 mm/year. They observed that recharge increased with increasing nitrogen fertilizer application and that these fluxes might have been overestimated by up to 20% based on anion exclusion measurements from adjacent soil cores. A possible explanation for the correlation between water flux and nitrogen applied was attributed to the fact that the more vigorous plants produced by the higher nitrogen rates might have probably created a soil structure with greater infiltration and less runoff.

Saghravani *et al*., (2013)used empirical method and obtained recharge of 12% of annual precipitation in tropical zone in Malaysia. They observed in their work that, climatic parameters and groundwater recharge showed positive and negative relationships with the highest correlation found between precipitation and recharge. They also observed that recharge and measured climatologic data had significant relationship with rainfall and wind speed.

Using stable isotope tracers in the monsoonal belt of West Africa,Geirnaert *et al*., (1984) and Adanu, (1991) observed that, the source of recharge was from the direct infiltration of rain water at the soil surface. They however, did not quantify the rate of recharge to the aquifer or confirm the timing of recharge events.

In the Sahel region, Northwest of Senegal, Edmunds and Gaye (1994)also obtained recharge rate of 1.7 to 11.7% of annual rainfall using chloride mass balance method. In another study Gaye and Edmunds, (1996) used chloride and tritium profiles and estimated recharge of 10 and 8% respectively of the mean annual rainfall in sands of North-western Senegal. Thiery (1988) estimated recharge rates between 5 and 8% of the mean annual rainfall in Ouagadougou, Burkina Faso using lumped parameter model approach.

In Ghana,Adomako (2010) reported varying recharge rate in the Densu River Basin between 30 and 182 mm/annum using water balance approach (using hydro meteorological data), numerical modeling and environmental isotope (δ^2H, δ^{18}O) profiles in the unsaturated zone.

Obuobie, (2008) used water table fluctuation measurements in the Volta basin and obtained recharge rate of 7 to 8% of the annual rainfall for 2006 to 2007 whiles chloride mass balance estimated the long term groundwater recharge rate of 8% of the mean annual rainfall. The soil water assessment tool (SWAT) model yielded recharge rate of 7% of the annual rainfall in the White Volta basin.

In the Voltaian System which consists of medium grains sandstones, micaceous sandstones, interbedded mudstones, siltstones and shalesYamoah (2013) used the chloride mass balance and water table fluctuation techniques to estimate recharge in Gushiegu. The chloride mass method suggested recharge in a range of 13.9 to 218 mm/year with an average of 89 mm/year which translated into about 1.3% to 21.8 % of the annual precipitation with an average of 8.9%. The water table fluctuation technique also yielded a cumulative average groundwater recharge of 71.4 mm/year and 81.0 mm/year which translated into 7.14 and 8.1% of the annual precipitation.

The low recharge rate was attributed to the geological characteristic of the unsaturated zone material.

In a different study, Pelig-Ba, (2004) used water balance (including hydrograph) and chloride mass balance to estimate recharge in the Pwalugu-Nawuni and in the Lawra-Bui catchments. The water balance method produced values of 1.4% of annual rainfall in the Pwalugu-Nawuni and 4.1% in the Lawra-Bui catchment.The chloride mass balance method estimated recharge of 4.5% of mean annual rainfall. This value as reported by Pelig-Ba, (2004)might not be enough to replenish the groundwater in the area.

Martin, (2006) used water balance, chloride mass balance, soil moisture and water level fluctuation methods and obtained recharge of 2 to 13% of mean annual rainfall in the AtankwidiCatchment. The long term recharge rate was determined by the chloride mass balance to be approximately 6% of average annual rainfall. Martin, (2006) observed in his study that, the intensity of rainfall had influence on recharge and that interannual comparison of water level fluctuations showed that a decrease in annual rainfall of about 20% caused a reduction of groundwater recharge of about 30 to 60%.

Among all these methods, water balance and the chloride mass balance are probably the most used method for the estimation of recharge in arid and semiarid regions. Examples can be found in (Allison and Hughes, 1983; Gaye and Edmunds, 1996; Edmunds *et al*., 2002; Lee *et al*., 2006; Martin, 2006; Yeh *et al*., 2007; Adomako, 2010; Marei *et al*., 2010). This is because perhaps these methods are easy and cheap methods to use. They also are very simple to use and can be applied in less sophisticated environments hence the reason to use these methods. Allison *et al*.,

(1994) and Phillips, (1994) cautioned against the use of numerical models to estimate recharge in semiarid environment. This is because diffuse recharge rates in such areas can be quite small relative to precipitation and evaporation. They are therefore, very sensitive to uncertain model parameterizations and input errors. Allison *et al*., (1994) for this reason, favour the use of environmental tracers for the estimation of groundwater recharge in semiarid environments. Natural tracers such as meteoric chloride are particularly popular due to their ubiquitous availability and increased sensitivity at lower recharge rates (Ng*et al*., 2009).

3.1.2 Water Balance Method (WBM)

The water balance group of methods estimates recharge as the residualof all other fluxes based on the principle that other fluxes can be measured or estimated more easily than recharge (Sophocleous, 2004). Some examples of water balance methods (WBM) are soil-moisture budgets, River-channel water balances and water-table rises (Sophocleous, 2004).Detailed reviews of these methods are provided by Sophocleous, (2004).The water balance method is generally based on the principle that precipitation in the form rainfall or snow fall must equal evaporation and river or groundwater outflow (baseflow) plus changes in soil moisture, groundwater and channel storage (Adomako, 2010). The water balance model in a catchment can be related to the input-output expression (Pelig-Ba, 2004;Adomako, 2010) as:

$$\boldsymbol{Input = Output - Storage} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(.)}$$

Putting into measureable quantities this equation becomes:

$$\boldsymbol{P = Qs + ET + R + \Delta S} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(.)}$$

Where P is precipitation, Qs is surface runoff, ET is evapotranspiration, R is mean annual recharge and ΔS is the change in mean storage.

ΔS is an important yet a difficult factor to determine because its value is dependent on antecedent conditions. It determines how much input is required to generate$R$. However, studies have shown on yearly basis that, in semiarid regions the value of ΔS is approximately zero. That is to meanthat, each year the soil-water contentconsistently returns to the same minimum value (Seyfried and Wilcox, 2006). This observation is buttressed by the fact that, potentialevapotranspiration greatly exceeds precipitation on an annual basis in semiarid regions(Adomako, 2010). Johnson and Law, (1991) also defined the storage component to comprise of soil moisture and groundwater storage which over a long period of time, becomes negligible with reference to precipitation and stream flow. Therefore it can be ignored.Several researchers have used the WBM to estimate recharge (Pelig-Ba, 2004; Lee *et al*., 2006; Martin, 2006; Yeh *et al*., 2007; Adomako, 2010). Different authors have used different approaches to estimate the **Qs** component of Equation 3.2. For example, Pelig-Ba, (2004)used hydrograph separation to estimate **Qs** in crystalline basement in northern Ghana. The estimation of **Qs** from hydrograph requires the separation of baseflow from quickflow or simply surface runoff. Adomako, (2010) also applied the Schreiber equation (described under methods) to estimate **Qs** southern Ghana in similar environment. This method is simple to use compared to the hydrograph separation, require simple climatic data and can easily be done in a spreadsheet hence was applied in this study.

The WBM requires basically meteorological variables such as air temperature and precipitation as well as knowledge on the vegetation and soil types within the area.Hence, this method is relatively convenient to use in terms of computation (Lee *et al.*, 2006).It is also very simple and easy to use in any water shed and less expensive to use.Seyfried, (2003) and Seyfried and Wilcox, (2006) outlined there major merits of using WBM in groundwater recharge estimation. These are: (i) it provides a framework that explicitly incorporates all factors affecting water supply, (ii) it uses storage (capacitance) parameters that are relatively easy to quantify and are amenable to functional modelling approaches suitable for large-scale management and (iii) it can easily incorporate deterministic spatial variability (Seyfried, 2003; Seyfried and Wilcox, 2006). The major setback in using this method is associated with the several assumptions and errors made in the calculation of potential evapotranspiration, surface runoff and soil moisture.

3.1.3Chloride Mass Balance (CMB)

Chloride is a conservative environmentaltracer, which indicates evaporation and monitoring its concentration in the environment can be used to estimate groundwater recharge (Kinzelbach *et al.*, 2002). Environmental tracers are dissolved substances introduced into the large scale water cycle by either natural means or by humans over long periods and are applicable in both saturated and unsaturated zones to estimate recharge (Kinzelbach *et al.*, 2002). In saturated zones, recharge is estimated from the difference of the chloride concentrations in rainfall and groundwater whereas in unsaturated zones recharge is calculated from the deviation of groundwater recharge from vadose zone pore water profile of chloride. Environmental chloride is deposited on land by atmospheric deposition processes through rainfall and dry fallout and is carried through the subsurface by infiltrating water. The fundamental assumption of the CMB method is based on mass conservation of chloride. Chloride ions do not significantly enter into oxidation or reduction reactions and it form no important solute complexes with other ions unless the chloride concentration is extremely high. It also does not form salts of low solubility and are not significantly adsorbed on mineral surfaces, and play few vital biochemical roles (Hem, 1985). The circulation of chloride ions in the hydrologic cycle is largely through physical processes (Hem, 1985).The CMB method has been applied in many arid and semiarid regions to estimate recharge (Allison et al., 1994; Gaye and Edmunds, 1996; Ting et al., 1998; Tyner et al., 1999; Zhu et al., 2003; Pelig-Ba, 2004; Martin, 2006; Adomako, 2010; Afrifa, 2013).

Chloride concentrations in unsaturated zone pore water are inversely related to recharge that is, high chloride concentrations indicate low recharge rates because chloride accumulates in the subsurface as a result of evapotranspiration whereas low chloride concentrations indicate high recharge rates because chloride is flushed through the subsurface (Afrifa, 2013). The assumptions necessary for successful application of the CMB method are: (i) atmospheric deposition is the only source of chloride (Cl^-) in groundwater (ii) Chloride is of a conservative nature in the system meaning that the ion neither leaches from, nor is absorbed by aquifer sediments and does not participate in any particular chemical reaction, (iii) surface run-on and runoff is negligible (Zhu, *et al*., 2003; Marei *et al*., 2010) (iv) the depth of the groundwater table should be deep enough to prevent groundwater evaporation (Zhu, *et al*., 2003; Marei *et al*., 2010)

By using this method, recharge in mm/year (R) can be estimated by equation (1) as described by Marie *et al*., (2010).

$$\boldsymbol{R = P \times \frac{Cl_p^-}{Cl_{gw}^-}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\mathbf{(.)}$$

Where, $\boldsymbol{P}$ is rainfall (mm/year); $\boldsymbol{Cl_p^-}$is weighted average chloride concentration in rainfall (mg/L); and $\boldsymbol{Cl_{gw}^-}$ is average chloride concentration in groundwater (mg/L).

The CMB method is cheap and can be carried out in less sophisticated laboratories because it requires simple data. However, it may not be applicable in several instances specifically in situations where there are other sources of chloride (for instance halites) in the soil other than the chloride contained in the rainwater. Also, recycling of dried salt by wind, unaccounted runoff and uptake by harvested plants may also affect the results (Kinzelbach, *et al*., 2002).

3.2Geochemical Studies

Geochemical studies provide knowledge on the distribution and concentration of elements in and between the different parts of the environment. It also helps in understanding the origin or source of pollution (Gałuszka and Migaszewski, 2012). The main aim of geochemical studies with respect to groundwater studies is concerned with identifying anomalies arising from geogenic and anthropogenic sources, the origin and evolution of groundwater(Adomako *et al*., 2010).Not only that, geochemical studies play key role in identifying and understanding the factors and processes that control the quality of groundwater in an area. The use of geochemical methods has proved to be an effective tool for assessing the groundwater evolution and movement. It also helps in identifying the source(s) of dissolved ions as well as the process(es) that lead to their release into groundwater (Edmunds *et al*., 2002, 2003; Lakshmanan *et al*., 2003; Adomako *et al*., 2010)

The chemistry of groundwater depends on a several factors including geology, the different hydrogeochemical processes that take place in the subsurface andanthropogenic activities. Studies have shown that the complexity of groundwater quality results from these factors and their interactions(Freeze and Cherry, 1979; Hem, 1985; Subramani *et al.*, 2005; Bhagavathi and Thamarai, 2008; Srinivasamoorthy *et al.*, 2012).The main mechanisms that control water chemistry include atmospheric precipitation, rock water interaction and evaporation-crystallisation(Gibbs, 1970).

Cartwright *et al*., (2004) also usedhydrogeochemical and isotopic techniques to study the origins of dryland salinity of Murray Basin, Victoria, Australia. The study showed that the chemistry of groundwater of low salinity in the area was controlled mainly by dissolution of silicate minerals whiles those of higher salinity groundwater in the area was controlled largely by mixing of groundwater, and evaporation as a consequence of a shallow water table.

Liu *et al*., (2003) attributed the major cause of groundwater salinization and arsenic pollution in the coastal area of Yun-Lin, Taiwan, to over extraction of groundwater. They explained that over-pumping of the local groundwater caused land subsidence and gradual salinization by seawater. Also, the introduction of excess dissolved oxygen oxidized the immobile minerals, and thereby released arsenic in the groundwater by reductive dissolution of arsenic-rich iron oxyhydroxides.

Kazemi and Mohammadi (2012) carried out hygrogeochemical studies in Safi Abad watershed in the north-eastern Iran to investigate the groundwater quality and the factors that controlled the quality. Their research showed that rainfall percolating into the mountainous areas of Safi Abad watershed remained mostly fresh while moving in the subsurface environment in the same mountainous area. However, the quality of resulting groundwaters deteriorated rapidly as it discharged into the adjoining plain as a result salinization. Different hydrogeochemical techniques employed showed that a variety of factors led to the severe salinization of groundwater in the plain. These included saline water intrusion, leaching of local saline soils into underlying groundwater, intense evaporation and slow rate of groundwater movement and over exploitation of the groundwater resources in the area.

Subramain *et al*., (2010) usedhydrochemical techniques such as Gibbs plot and bi-plots of major ions andreported that the predominant factors affecting the groundwater chemistry in Chithar River basin included weathering of carbonate and silicate minerals, ion exchange reactions and the impact of agricultural activities such as irrigation return flow and fertiliser application.

In Cuddalore Coastal Area, Tamilnadu, India, Senthilkumar *et al*., (2012) also identified seawater intrusion and anthropogenic activities as the hydrogeochemical processes controlling the groundwater quality. Sami (1992) used stable isotope (^{18}O and ^{2}H) and geochemical signatures to investigate recharge processes and groundwater salinization mechanisms in a semi-arid rangeland catchment in Eastern Cape, South Africa. From the study, chloride and isotopic relationships suggested that chloride ions in groundwater were of meteoric origin. The salinization mechanism was attributed to evaporative enrichment and leaching of surficial meteoric salts into groundwater. The result further showed that, meteoric sodium chloride contributed more than 90% of the dissolved sodium, except at low salinities, where cation exchange processes contributed additional sodium inputs in exchange for dissolved calcium and magnesium.

Abd Alla, (2008) however, identified seepage of irrigation water, sanitary water and other domestic water as the main causes for groundwaterpollution in certain parts of south Giza, Egypt.The concentration of ions in groundwater in Southwest Sinai, Egypt was attributed to the dissolution of carbonate and sulphate minerals in the aquifer matrices and recharge areas and cation exchange reactions (El-Fiky, 2010).

Manoj *et al*., (2013) used multivariate and hydrostatistical methods together with conventional hydrochemical (graphical) techniques to successful characterise and classify the hydrochemistry of the some water bodies.Huang *et al*., (2014) used multivariate analytical methods such as principal components analysis and hierarchical cluster analysis to evaluate the groundwater quality in south China.

Multivariate statistical techniques such as factor analysis were applied by(Rao *et al*., 2013) to identify the major factors (variables) corresponding to the different source of variation in groundwater quality. The study showed that water quality of groundwater was influenced by both anthropogenic activities and chemical weathering and that the most serious pollution threat to groundwater was from TDS, Cr^{6+} and Fe^{2+} associated with sewage and pollution of tannery waste.

Okiongbo and Douglas, (2014) also used PCA, factor analysis and graphical techniques to assess the groundwater quality in Southern Nigeria and observed that the natural weathering of existing silicate rocks, reverse ion-exchange processes and oxidation reactions were the main sources of dissolved ions in groundwater in the area.

Principal component analysis, Piper graphical classification together with stable isotope (^{18}O and ^{12}H) of groundwater and surface-water samples were used by Kortatsi *et al*., (2009) to delineate geochemical processes and groundwater facies in Kulpawn Basin in northern Ghana. It was reported that groundwater composition in the Kulpawn basin was largely controlled by aluminosilicates (such as plagioclase, pyroxene and biotite) dissolution and cation exchange resulting in mainly Ca-Mg-HCO_3 and Na-HCO_3 water types.

Anku *et al*., (2008) investigated the quality of groundwater from fractured rock aquifers in the northern parts of Ghana. On the basis of activity diagrams, they observed that all groundwater samples were stable in the montmorillonite field, suggesting silicate mineral weathering. Hydrochemical studies revealed that groundwater from these aquifers were generally within acceptable limits for most domestic uses. However, there were occurrences of high-nitrate concentrations (50–194 mg/l) in some of the boreholes in the western section of the area. The increased level of nitrate was attributed to anthropogenic impact on the groundwater.

Zakaria *et al*., (2012)studied the hydrogeohemistry of the Ayensu River Basin. Their study showed that groundwater in the area was fresh and the dominant water types were Na-Cl and Na-HCO_3-Cl. They attributed the occurrence of these facies to the dissolution of soluble salts in the soil horizon and aerosol spray. The occurrence of major ions like Na^+, Cl^-, K^+, Ca^{2+}, Mg^{2+} and SO_4^{2-} in the groundwater was also found to be probably caused by sea aerosol spray and decay of organic matter.

Adomako*et al*., (2010) used hydrochemical and multivariate analyses to investigate the geochemistry, evolution of groundwater as well as its characteristics recharge processes and estimation in the Densu River Basin. Their study showed that, groundwater chemically evolved from Ca-HCO_3, Ca/Mg- HCO_3 to Ca/Na-Cl, Ca-Na-HCO_3, and Na-Cl. The evolution was reported to be controlled by processes such as weathering of silicate minerals, carbonate dissolution, ion exchange and slight evaporation which seem to be more pronounced down gradient of the flow system.

3.3 Water Quality Studies

The quality of water is as important as it availability because it determines its intended use(Bhagavathi and Thamarai, 2008). It has been reported that, the use of water in general for various purposes such as domestic, irrigation and industrial to a large extent is determined by it chemistry (Hem, 1985). Therefore monitoring the water quality in aquatic systems plays significant role in the water quality control (Khwakaram *et al*., 2012).

Several studies on groundwater quality for various purposes have been carried across the globe. The emphasis of majority of such works is on groundwater quality for domestic and irrigation uses. Examples can be found in (Pelig-Ba *et al*., 1991; Kumar *et al*., 2006; Anku *etal*., 2008; Ansa-Asare *et al*., 2009; Kortatsi *et al*., 2009; Pelig-Ba, 2009; Abugri and Pelig-Ba, 2011; Brindha and Elango, 2011; Ramesh and Bhuvana, 2012; Senthilkumar and Elango, 2013).

Ramesh and Bhuvana, (2012) sampled thirty groundwater samples in Periyakulamtaluk of Theni district in Tamil Nadu, India with an objective of understanding the suitability of local groundwater quality for domestic and irrigation purposes. The outcome of the study showed that groundwater in this area was found to be within the acceptable limits of Bureau of Indian Standards (BIS) for drinking water although hardness and fluoride level exceeded the permissible limit in some locations. They reported that, the presence of fluoride above the permissible level posed a serious threat to rural population as dental fluorosis appeared at alarming rate in certain regions. Most of the groundwater samples were suitable for irrigation except in a few locations on the basis of salinity ,chloronity, sodicity indices, sodium percentage, and residual sodium carbonate.

Balan *et al*., (2012) also assessed groundwater quality in Chennai, Tamil Nadu, India using water quality index. The results showed that, except for pH, the groundwater quality assessment parameters were within the accepted standard values of BIS and the groundwater quality status of Chennai city ranged from excellent to good for human consumption based on all the nine parameters of water quality index.

Rao *et al*., (2013) conducted a study to assess the groundwater pollution and identify major variables affecting the groundwater quality in Ranipet industrial area by monitoring twenty five wells during pre- and post-monsoon in 2008. Analysis of the major physico-chemical parameters showed increased total dissolved solids (TDS), Iron (Fe^{2+}) and Hexavalent Chromium (Cr^{6+}) above the WHO guideline levels for drinking-water for most of the samples making them potentially unsafe for drinking.

In the northern region of Ghana, Kortatsi *et al*., (2009) investigated the groundwater quality in the Kulpawn Basin for domestic and irrigation uses. Their findings showed that, the groundwater quality was generally good for domestic purpose based on the hydrochemistry. However, 18 and 47% out of 92 boreholes sampled respectively had NO_3^- and F^- levels outside WHO allowable limits suggesting potential physiological problems in some localities. The groundwater had low sodium absorption ratio and low to moderate salinity hazard but significant magnesium hazard partially limiting its use for irrigation.

Pelig-Ba, (1998) investigated the trace elements composition in groundwater samples from sixty boreholes in the Upper East and West Regions of Ghana. His report indicated that the concentrations of most trace element analysed were higher as compared to their concentrations found in natural water systems particularly Al, Fe, Mn, Zn, Sr, and Ba concentrations were found to be extremely high compared with WHO guidelines for drinking-water.

In another study, Boah *et al*., (2015) applied Water Quality Index (WQI) to assess the suitability of Vea Dam for drinking purposes. They used ten physico-chemical parameters namely pH, EC, TDS, total hardness, nitrates, sulphates, chlorides, calcium, dissolved oxygen (DO) and biochemical oxygen demand (BOD) in their assessment and found the water not suitable for drinking with WQI of 54.21.

Barnie *et al*., (2014), also assessed the groundwater quality for irrigation in the Atankwidi catchmentand reported that, the groundwater quality was suitable for irrigation based on the pH, sodium and salinity hazards. However, some samples showed potential magnesium hazard, and alkalinity thereby limiting its use for irrigation.

3.3.1 Water Quality Index

Water quality index, is a very essential tool in the assessment of the suitability of water quality. It is the parameter which translates the information on overall water quality into a form that can easily be understood and appreciated (Khwakaram *et al*., 2012). It is dimensionless value and combines multiple water-quality factors into a single number by normalizing values to subjective rating curves. Parameters in WQI models vary based on the intended uses and local preferences(Khwakaram *et al*., 2012).

Commonly used water quality indices include Canadian Council of Ministers of Environment (CCMEWQI), National Sanitation Foundation (NSFWQI), British Columbia (BCWQI), Oregon (OWQI), Overall Index of Pollution (OIP), Bhargavamethod, Smith's index, The River Ganga Index, Tiwari and Mishra index, and Stigter index (Tomer, 2015). Detailed review of the various water quality indices are provided by (Bharti and Katyal, 2011; Tomer, 2015).

Generally, WQI is defined for a specific and intended use of water. In this study, the WQI of groundwater was determined for domestic use. Cude (2001); Khwakaram *et al*., (2012) and Balan *et al*., (2012) calculated WQI for domestic use using the Arithmetic Weighted Method.Khwakaram *et al*., (2012) used water quality parameters like pH, EC, dissolved oxygen (DO), turbidity, total hardness (TH), calcium, magnesium, sodium, potassium, chloride, sulphate, nitrate and phosphate. They concluded that, the water quality rating at most of the sampled water were outside the WHO standards for drinking-water unsuitable for the human uses during the period of study.

Deepak and Singh, (2013) on the other hand used turbidity, pH, total alkalinity, total dissolved solids (TDS), hardness, sulphate, chloride, fluoride and nitrates whereas Balan *et al*., (2012) used pH, TDS, turbidity, total hardness, calcium, magnesium, sulphates, chlorides, and nitrates. The parameters in ten bore wells from different localities in Dhar town were monitored seasonally during the study period. Results obtained from the study revealed that WQI during each season is well within the permissible limit and that the groundwater was safe for drinking.

CHAPTER FOUR

MATERIALS AND METHODS

4.1 Field Methods

4.1.1 SampleCollection

The samples collected for this work includedrainwater and groundwater samples. The parameters analysed in samples were Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^-, and HCO_3^- as major ions whiles the trace elements included Pb, Cd, As, Zn, F^-, Cu, Sb, Cr, Co, Fe, Ni and Mn.

Seventeen (17) rainwater samples were collected from rain gauge used by the Navrongo Meteorological Station which is the nearest station to the study area during 2013 and 2014 rainy seasons from May to October each year into plastic bottles. Prior to sample collection, the bottles were washed with detergent to remove all traces of contaminant and rinsed thoroughly with distilled water and dried. Rainwater samples were collected immediately after each rainfall event from the rain gauge after recording the amount of rainfall. Samples collected were filtered with 0.45 µm filter papers into the pre-washed and rinsed plastic bottle containers and stored in the fridge at temperature of about 4℃ for laboratory analysis. The sample bottle was first rinsed with portion of the sample water each time to remove any possible traces of contaminant before samples were transferred into it.

Groundwater samples were collected from 50 boreholes equipped with hand pumps within the Atankwidi Catchment in April, 2014. The samples were collected after continuous pumping for about ten minutes to purge any stagnant water around the pump except in cases where there was pumping of water from the wells on arrival at the sampling point. Before the samples were collected, the bottle was rinsed thoroughly with water from the borehole.

Two (2) samples were collected at each sample point into plastic bottles. One sample was acidified with concentrated nitric acid (about 2 or 3 drops) to a pH of about 2 and the other left un-acidified. The acidified samples were used for the analyses of cations whiles the un-acidified samples were used for the analyses of anions. The acidification was to prevent the possible precipitation, flocculation and/or sorption losses of cations to the walls of the containing vessels. In addition, the GPS location (in UTM) for each sample was recorded. The sampling locations are as indicated in Figure ..

4.1.2 Measurement of Field Parameters

Physical parameters like temperature, pH, total dissolved solids (TDS) and electrical conductivity (EC) as well as the bicarbonate (HCO_3^-) alkalinity whose value can be influenced by changes in environmental conditions were determined in the field.

The temperature, pH and EC were measured with a multifunction portable meter XLS1005 manufactured by Itech. The TDS was determined with a hand held TDS meter (model no: TDS-EZ made in China). The HCO_3^- was determined by titration.

Methyl orange indicator was prepared by dissolving 0.125 g of methyl orange in 250 mL standard flask with distilled water and made up to the mark. It was subsequently transferred into the indicator bottle and stored for analysis.The bicarbonate alkalinity, was determined by pipetting 50 mL of the sample into a conical flask and applying two (2) drops of methyl orange indicator.

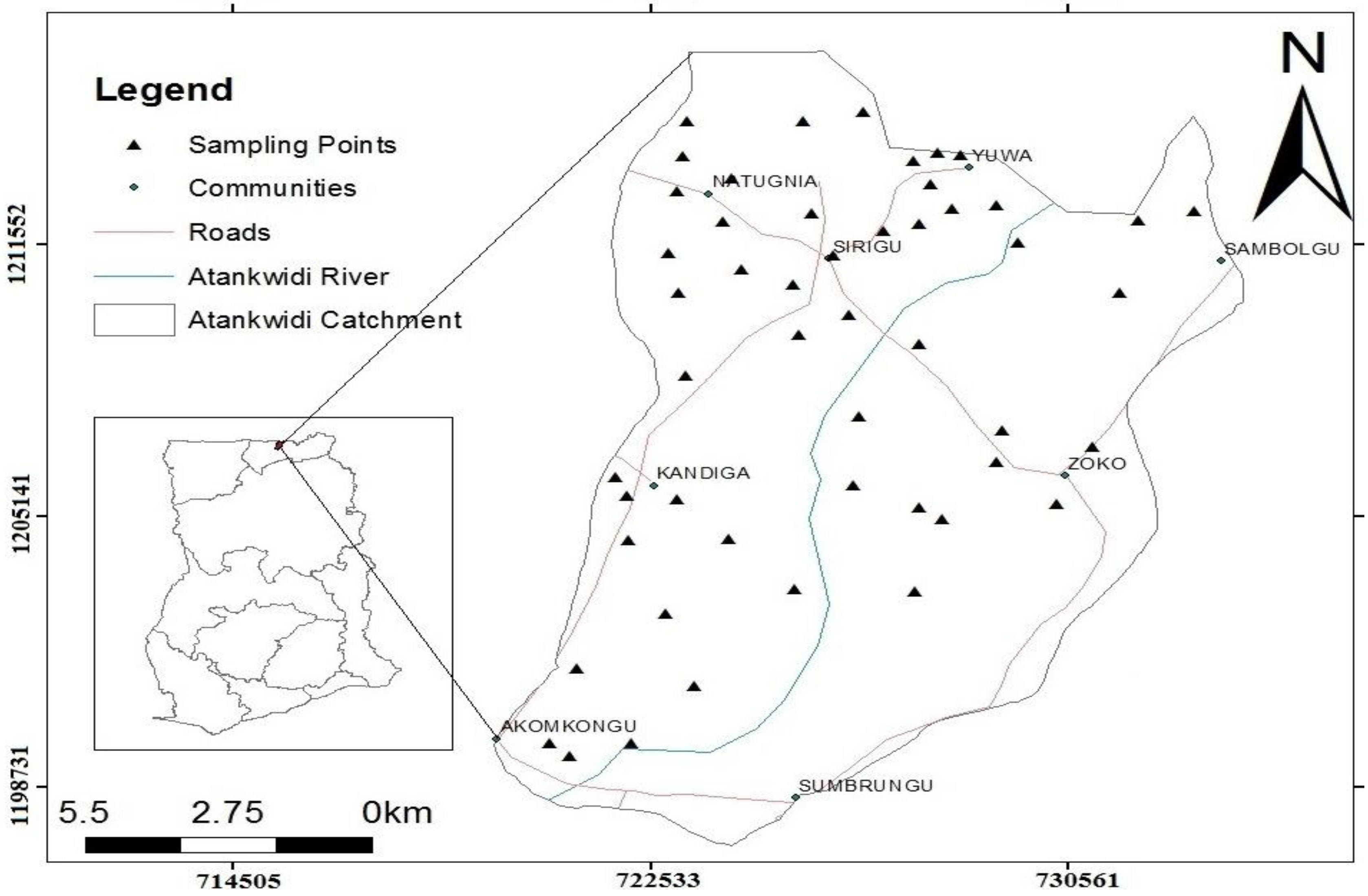


Figure .: Groundwater sampling locations in the study area.

The sample was then titrated against standard 0.01M H_2SO_4 until the yellow colour turned orange. The change in colour from yellow to orange indicated the end point and the volume of H_2SO_4 used was recorded as titre value. The procedure was repeated three times and averaged titre calculated (APHA, 1998).The titration was carried out on the field because HCO_3^- easily decomposes.

Calculations

The reaction equation is given by Eaquation 4.1.

$H_2SO_4 + CaCO_3 \rightarrow H_2O + CO_2 + CaSO_4$ .... (.)

$\mathbf{Carbonate\ Alkalinity\ as\ CaCO_3(mg/L)} = \frac{\mathbf{C_A \times V_A}}{\mathbf{V_S}} \times \mathbf{M} \times \mathbf{100}$…………..(.)

$\mathbf{Alkalinity\ as\ HCO_3^-(mg/L) = Carbonate\ Alk\ as\ CaCO_3(mg/L) \times 1.2}$ …...… (.)

Where C_A is the molarity of H_2SO_4, V_A is th average volume of acid H_2SO_4used,V_S is the volume of sample used and M is the molar mass of $CaCO_3$.

4.2 Estimation of Recharge

4.2.1 Water Balance Method (WBM)

Monthly rainfall (mm), temperature (°C), humidity (%), sunshine hours and wind speed (m/s) data were obtained from the Ghana Meteorological Service, for Navrongo from 1983 to 2015.These data sets were used to estimate components in the simplified conceptual model depicted in Figure 4.2.Recharge to the groundwater by WBM was calculated using the simplified water balance equation (Equation 4.4):

$\boldsymbol{R = P - ET_o - Q_s}$ ……………………………………………………………**(.)**

Where, $\boldsymbol{R}$ is the groundwater recharge (mm), $\boldsymbol{P}$ is the annual rainfall (mm), $\boldsymbol{ET_o}$ is potential evapotranspiration (mm) and $\boldsymbol{Q_s}$ is the surface runoff (mm). The value of$\boldsymbol{ET_o}$was estimated from minimum and maximum daily temperature (°C), humidity

(%), sunshine hours, wind speed (m/s) values using the computer programme CROPWAT 8.0 Bèta.

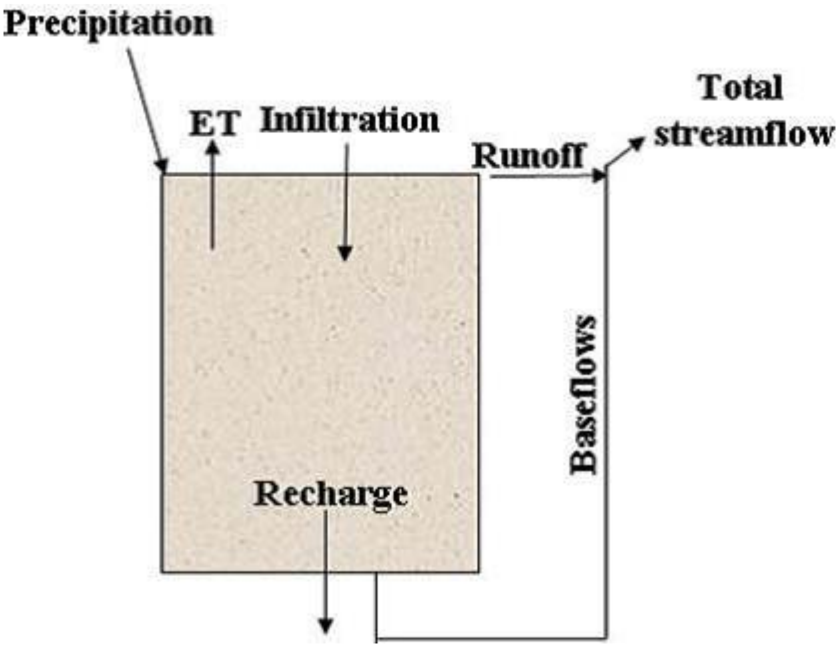


Figure .: Conceptual model for the watershed water budget showing various hydrologic processes (Adomako, 2010)

The Q_s component of the equation was determined by applying the Equation 4.5(Schreiber, 1904)

$$\boldsymbol{Q_s = 1000AP\left[exp\left(-\frac{e_o}{P}\right)\right]}\text{…………....……………………………………}\textbf{(.)}$$

$$\boldsymbol{e_o = 1.0\ x10^9 exp\left(\frac{-4.62\ x\ 10^3}{T+273.15}\right)}\text{…………………………………………………}\textbf{(.)}$$

Where **Q**$_s$ is the monthly surface runoff in m^3, **T** is monthly temperature in **K** and **A** is the catchment area in km^2 and **P** is precipitation in mm per month.

4.2.2 Chloride Mass Balance (CMB) Method

Recharge by the CMB method was determined by using Equation4.7

$$\boldsymbol{R = P \times \frac{Cl_p^-}{Cl_{gw}^-}}\text{ ………………………………………………………………}\textbf{(.)}$$

Where, $\boldsymbol{P}$ is rainfall (mm/year); $\boldsymbol{Cl_p^-}$is weighted average chloride concentration in rainfall (mg/L); and $\boldsymbol{Cl_{gw}^{-}}$ is average chloride concentration in groundwater (mg/L). The weighted average Cl_p^- was calculated according to the following equation:

$$\boldsymbol{Cl_p^-} = \frac{\boldsymbol{P_1 \times Cl_1 + \ldots\ldots\ldots + P_n \times Cl_n}}{\boldsymbol{P_1 + \ldots\ldots\ldots + P_n}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(.)}$$

Where $\boldsymbol{P_1}$ is the first rainfall event (mm) and $\boldsymbol{Cl}_1$ is the corresponding chloride concentration in the rainfall (mg/L), for 1 to n events (Marie *et al*., 2010).

4.3Laboratory Measurement

4.3.1Determination of Major Ions

a) *Determination of Sodium and Potassium*

Sodium (Na) and potassium (K) concentrations were analyzed using Flame Emission Photometer (FEP). The determination of Na in the samples was done at a wavelength of 589 nm whereas the level of K was determined at wavelength of 766.5 nm. The Flame Photometer was set based on the required element to be determined. Before each element was analysed, a blank solution and standards (2, 4, 6 mg/L) were aspirated into the FEP and a plot of standard curve of Na and K were obtained by plotting concentrations against emission intensities for each element. The water samples were then aspirated into the flame and the emission intensity recorded. The concentration of Na and K in the unknown samples were determined by reading the concentration of the sample which corresponded to its emission intensity from the calibration curve (Skoog *et al*., 2004)

b) *Determination of Calcium (Ca) and Magnesium (Mg)*

The concentration of Magnesium (Mg) and Calcium (Ca) were determined using the atomic absorption spectrophotometer (AAS). Before the analyses, the water samples were filtered and digested. For Mg, 1mL of the sample was pipetted into a test tube and 9 mL of lanthanum solution was added as a suppressant to dissolve the Mg ions in solution. The Mg levels in the sample were ready to be determined. The digestion of Ca was carried out by pipetting 5 mL of the water sample into beaker in three replicate. Six millilitre (6 mL) of 65 % of concentrated HNO_3 was added to dissolve the metal in solution, followed by 3 mL of 35 % HCl and five drops of 0.25 % of H_2O_2 (catalyst) to each vessel containing the water sample. The beakers were swirled gently to ensure homogeneity and subsequently digested in a microwave digester for 20 minutes. After digestion was completed, the solutions were cooled down in water bath for twenty (20) minutes inside a fume hood. Cooling the digested sample was necessary to reduce high temperature and pressure build-up within the vessels. The mixture was then transferred quantitatively into volumetric flask and diluted to 20 mL using deionised distilled water and made ready for AAS analysis. Prior to the analyses of the samples, the AAS was calibrated with blanks and standard solutions of 0.1, 0.2, 0.4, 0.6 Mg/L of each the analyte. The blank was treated in the same way as the sample except that it did not contain the analyte. Calibration curves were drawn by running standards of various concentrations on the AAS and plotting their concentrations against absorbencies. The samples were the aspirated and measured and the concentration of Mg and Ca in the samples measured against the appropriate calibration curve.

c) Determination of Chloride (Cl^-)

The level of Cl^- in the water samples were determined by Argentometric titration (the silver nitrate) method using potassium chromate as indicator. To prepare potassium chromate (K_2CrO_4) indicator, 50.0 g K_2CrO_4 was weighed and dissolved in 250 mL distilled water. Drops of $AgNO_3$ were added to the K_2CrO_4 solution till definite red precipitate formed. This was necessary to make sure that, any available Cl^- that may be present was removed.The solution was allowed to stand undisturbed over night after which it was filtered and subsequently diluted to 1000 mL in a standard flask. Silver nitrate ($AgNO_3$) solution of 0.0141 M was prepared by dissolving 2.395 g of $AgNO_3$ in 250 mL distilled water and subsequently diluted to 1000 mL. The resulting solution was standardised against, 0.0141 M sodium chloride (NaCl). The 0.0141M concentration of NaCl was prepared by dissolving 8.24 g of NaCl dried at 40°C in distilled water and diluted to 1000 mL in a standard flask. To determine the Cl^- concentration of the samples, a volume of 100 mL each of the sample was pipetted into a conical flask. A volume of 1.0 mL potassium chromate indicator was added to each sample and titrated against standard $AgNO_3$ solution until a pinkish yellow endpoint. The volume of $AgNO_3$ used at the equivalence point was recorded. The process was repeated twice to obtain a consistent titre value. Distilled water (100 mL) was titrated in the same way to establish reagent blank (APHA, 1998).

Calculation

$$\text{Chloride mg/L as } Cl^- = \frac{\mathbf{(A-B)\ x\ C\ x\ 35.45}}{\mathbf{V_s\ (mL)}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(.)}$$

Where, A = volume (mL) of $AgNO_3$ required for sample, B = volume of mL $AgNO_3$ required for blank, c = concentration of $AgNO_3$ used and V_s= volume of sample used.

d) Determination of Fluoride (F^-)

Fluoride was determined by Sulfophenylazodihydroxynaphthalene-disulfonate(SPANDS) method. SPANDS solution was prepared by dissolving 958 mg of sodium 2- (parasulphophenylazo)-1,8-dihydroxy-3,6-naphthalenedisulphonate (SPANDS reagent) in distilled water and diluted to 500 mL. This solution was stored in dark bottles and kept away from light as possible to prevent decomposition. Zirconyl acid reagent was also prepared by dissolving 133 mg $ZrOCl_2.8H_2O$ in 25 mL water. 350 mL of concentrated HCl was added to it and diluted to 500 mL with distilled water. Equal volumes of 500 mL of Zirconyl acid reagent and SPANDS solution were mixed to produce a single reagent (Acid Zirconyl-SPANDS). This solution was stored in dark bottles and kept away from light as possible to keep it fresh. A reference solution which was used to set the spectrophotometer to zero absorbance was prepared by diluting 10 mL SPANDS solution to 100 mL with distilled water. Seven millilitres (7 mL) concentrated HCl was diluted to 10 mL with distilled water and added to the dilute SPANDS solution. Sodium arsenate ($NaAsO_2$) 5.0g was dissolved in distilled water and diluted to 1000 mL. A stock fluoride solution of 100 µgF^- was prepared by dissolving 221 mg anhydrous NaF in distilled water and made up to 1000 mL.Standard F^- solution of was prepared by diluting 100 mL stock F^- solution to 1000 mL with distilled (1 mL = 10µg F). Calibration standard solutions of 1, 2, 5, and 10 µg F^- were prepared by diluting 0.1, 0.2 0.5 and 1.0 mL of standard stock of F^- to 50 mL. A volume of 50 mL each from the working standard was pipetted into 50 mL Nessler tubes. Volume of 10 mL of the mixed acid-Zirconyl-SPANDS reagent was pipetted and added to each standard and mixed well. Two to three drops of $NaAsO_2$ were added to remove any residual chloride that may be present. The spectrophotometer was set to zero absorbance with the reference solution at 570 nm. A standard calibration curve of concentration against absorbance was plotted. 50 mL each of the sample was pipetted into 50 mL Nessler tubes and treated in the same way as the standards. The absorbance of each sample was then read using the spectrophotometer at the same wavelength. The concentration of F^- in each sample was extrapolated from the standard curve graph.A volume of 10 mL of the sample was pipetted and diluted to 50 mL with distilled water 10.00 mL acid-zirconyl-SPADNS reagent, mix well to develop the colour. The reference point of photometer as above and the absorbance of the developed was colour read at same wavelength (APHA, 1998).

Calculation

$$\boldsymbol{F^{-}(mg/L) = \frac{A}{B}\ x\ \frac{1}{R}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\mathbf{(.)}$$

Where: A = µg F- reading from the standard curve, B = volume of diluted or undiluted sample taken for colour development, mL R = when sample is diluted, volume of sample taken for dilution/final volume after dilution.

e) *Determination of Nitrates (NO_3^-)as NO_3^--N*

The concentration of nitrate in the samples was determined by ultra-violet (UV) spectrophotometer. A stock solution of 100 mg/L NO_3^--N was prepared by dissolving 0.7218g of anhydrous KNO_3 in 1000 ML of solution. A volume of 2 mL of $CHCl_3$ was added to the stock solution to preserve it. Standard solution of 10 mg/L NO_3^--N was prepared by diluting 100 mL of the stock to 1000 mL and 2 mL $CHCl_3$ added as preservative. Dilute hydrochloric acid of 1 M was prepared by diluting 83 mL of concentration HCl (36% W/V) to 1000 mL. Calibration standards of 0.2, 0.4, 0.8, 1.4, 2.0, 3.0, 5.0, 6.0 and 7.0 mg/L NO_3^--N was prepared by diluting 1, 2, 4, 7, 10, 15, 20, 25 30 and 35 mL respectively to 50 mL. To every 50 mL of the calibration standard, 1 mL of 1.0 M HCl was added and mixed thoroughly. The UV spectrophotometer was set to zero absorbance using distilled nitrate free water at 220 nm wavelength to obtain absorbance due $NO_3^-$and at 275 nm wavelength to determine the interference due to dissolved organic matter. The absorbance of each standard was then read and recorded. To obtain the absorbance due to nitrate, 2 times the absorbance value due to interference (absorbance at 275 nm wavelength) was subtracted from absorbance value at 220 nm wavelength. A standard curve of absorbance due to NO_3^- was plotted against the concentration of NO_3^--N in the calibration standards. To analyse the nitrate level in the samples, 50 mL each of the sample was measured and treated in the same way as the calibration standards to obtain the corrected sample absorbance. The concentration of the nitrate in each sample was directly obtained from the standard curve by extrapolation (APHA, 1998).

f) Determination of sulphates (SO_4^{2-})

A buffer solution was prepared by dissolving 30 g of magnesium chloride ($MgCl_2.6H_2O$), 5 g sodium acetate ($CH_3COONa.3H_2O$), 1 g potassium nitrate (KNO_3) and 20 mL acetic acid, CH_3COOH (99%) in distilled water and made up to 1000 mL. A stock solution of 100 mg/L SO_4^{2-} was prepared from anhydrous Na_2SO_4 salt by dissolving 1.4791 g of the salt in distilled water and made up to 1000 mL. A volume of 100 mL of the stock was diluted to 1000 mL to obtain a standard solution of 100 mg/L SO_4^{2-}. Calibration standards of concentrations of 5.0, 10.0, 15.0, 20.0 and 25.0 mg/L SO_2^{2-} were prepared by diluting 5, 10, 15, 20, and 25 mL respectively of the standard solution of SO_4^{2-} to 100 mL. A volume of 100 mL each of the calibration standards was pipetted into a 250 mL conical flask and 20 mL of the buffer solution added and stirred to mix thoroughly. While stirring, 1 spatula full of $BaCl_2$ was added. The solution was continuously stirred for one minute at constant speed after the addition of $BaCl_2$. The suspension was poured into a cuvette and the absorbance read using the spectrophotometer at a wavelength of 420 nm at 5±0.5 minutes. This procedure was repeated for a blank (no $BaCl_2$) was added to correct for sample colour and turbidity. A volume of 100 mL each of the sample was pipetted into a conical flask and treated in the same way as the calibration standards. The absorbance of the value of the blank was subtracted from that of the standards and the samples to obtain the absorbance due to SO_4^{2-}. A standard calibration curve was developed by plotting absorbance against theconcentration in the calibration standards. The concentration of SO_4^{2-} in the samples was directly extrapolated from the standard calibration curve (APHA, 1998).

4.3.2Determination of Trace Elements

The determination of trace metals (As, Cd, Cr, Co, Fe, Mn, Ni,Pb and Zn) levels in water samples were performed using the VARIAN AA 240 Fast Sequential (FS) Atomic Absorption Spectrometer equipped with a deuterium background corrector. Elemental As levels in the water samples were determined using Hydride Generation Atomic Absorption Spectrometry (HG-AAS); whereas Cd, Co, Fe, Ni and Pb levels were determined using Flame Atomic Absorption Spectrometry (FAAS).

Before each trace element was determined, water samples were digested on a hot plate for 3 hours in a fume hood. The digestion was done by pipetting 4.5 mL of concentrated HCl and 0.5 mL concentrated HNO_3 into 40 mL of water samples in a 100 mL borax glass beaker, and placed on a hot plate. After, the 3 hours the digested samples were made to cool, filtered and diluted with double distilled water to make a volume of 30 mL (nominal volume).

a)Determination of As by HG-AAS

Arsenic (As) concentration in groundwater was determined by hydride generation as described below.

Four millilitres of freshly prepared 5 M KI was added to the digested samples. This was done in order to reduce all As^{5+} to As^{3+}, represented by the Equation 4.10

$As^{5+} + 2I^{-} \rightarrow As^{3+} + I_2$……………………………………………………………...**(.)**

The continuous flow approach was used to merge sample solution and reagents. The sample solution of flow rate 0.1 mL/s was mixed with 0.1 mL/s each of HCl and $NaBH_4$ solutions in a polyetheretherketone (PEEK) cross connector and pumped into a reaction coil. During the mixing, hydride (AsH_3) and considerably hydrogen gas (H_2) are produce according to the Equations 4.11 and 4.12.

$3BH_4^- + 3H^+ + 4H_3AsO_3 \rightarrow 3H_3BO_3 + 4AsH_3 + 3H_2O$…………………………**(.)**

$BH_4^- + H^+ + 3H_2O \rightarrow H_3BO_3 + 4H_2$……………………………………………..**(.)**

The gaseous AsH_3 and H_2 generated were separated from the liquid phase and transferred with an argon gas flow and dried by a stream of nitrogen gas. Sub-stock solution of 10 mg/L was by prepared diluting 1 mL of stock solution with distilled water into 100 mL solution. Calibration standards (0.2, 0.4, 0.6, 0.8 and 1.0 mg/L) were prepared by diluting 2, 4, 8 and 10 mL of sub-stock solution with distilled water into 100 mL solution. These were used to calibrate the instrument. Samples were then aspirated into the atomic absorption spectrometer (AAS) and for every 10 readings a standard was aspirated as a quality control measure.

Calculation

The concentration of As in each water sample read from the AAS was used to calculate for the As final concentration of the water samples according the equation (3.12);

$$\boldsymbol{Final\ conc.\,(mg/L)} = \frac{\boldsymbol{Conc._{AAS}\ x\ Df\ x\ Nominal\ Volume\ (mL)}}{\boldsymbol{Sample\ Volume\ (mL)}}\text{……………………}\mathbf{(.)}$$

where, Df is dilution factor, and $Conc._{AAS}$ is concentration of As read from the AAS.

b) Determination of Cd, Co, Cr, Cu, Fe, Ni, Mn, Pband Zn, using FAAS

Sub-stock solution of 10 mg/L Cd was prepared by diluting 1 mL (Cd stock solution) with distilled water into a 100 mL solution. Also, 100.0 mg/L of Co, Cr, Cu, Fe, Ni, Mn, Pb and Zn were prepared by diluting 10.0 mL of Co, Cr, Cu, Fe, Ni, Mn, Pb and Zn stock solutions with distilled water into a 100 mL solution. Three (3) working standards 0.5, 2, 5 mg/L Cd were prepared by diluting 5, 20 and 30 mL each of Cd sub-stock solution with distilled water into 100 mL solutions. Three (3) working standards of 2, 5, 10 mg/L each of Co, Cr, Cu, Fe, Ni, Mn, Pb and Zn were prepared from the sub-stock solutions of Co, Cr, Cu, Fe, Ni, Mn, Pb and Zn. This were done by diluting 2, 5, 10 mL of each of sub-stock solution with distilled water into 100 mL solutions. These were used to calibrate the instrument.

The digested samples were then aspirated into the atomic absorption spectrometer (AAS) and for every 10 readings a standard was aspirated as a quality control measure. The concentration of Cd, Co, Cr, Cu, Fe, Ni, Mn, Pb and Zn in each water sample read from the AAS was used to calculate for their final concentrations in the water samples according the equation…

$$\boldsymbol{Final\ conc.} = \frac{\boldsymbol{Conc._{AAS}\ x\ Df\ x\ Nominal\ volume\ (mL)}}{\boldsymbol{Vloume\ of\ sample}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\mathbf{(.)}$$

where all terms are as defined in Equation 4.13.

4.4. Quality Assurance/Quality Control (QA/QC) Measures

The following set of operating principles wereobserved in order to help produce credible and reliable data.

All glassware and water sample containers were washed with detergent and rinsed with distilled water and subsequently dried before use. This was to ensure that the sample bottles were free from contaminants which could affect the concentrations of various ions in the water samples. Collected samples were labelled and recorded with the location. Boreholes were purged for ten minutes to flush the stagnant water around the pumps except in cases where there was pumping at the time of arrival. In the case of hand-dug wells, it was properly checked and confirmed that the dug well was constantly used. This was to ensure that stale and stagnant water was not sampled. To prevent deterioration all the collected samples were kept in ice (temperature of about 4°C) before transported to the laboratory. Parameters such as pH, bicarbonate, electrical conductivity and temperature which can easily deteriorate or whose value is easily affected by changes in environmental conditions were determined in the field immediately after sampling. All reagents used were of analytical grade. All instruments were calibrated with chemical standard solutions prepared from commercially available chemicals. Duplicates of samples were collect at some points to check for consistency of results. The accuracy of the laboratory analysis was checked by calculating the charge balance error and only those results within ±5% were relied on for subsequent interpretation.

4.5 Charge Balance Error (CBE)

The charge balance error was calculated for the groundwater samples. The fundamental condition of electrolyte solutions on macroscopic scale is such that solutions are electrically neutral (Freeze and Cherry, 1979). This implies that in groundwater the total sum of the positive charges (cations, in meq/L) must be equal to the sum of all the negative charges (anions, in meq/L). However, due to analytical errors and unanalysed constituents in the chemical analyses results in electrical imbalances. A measurement of this imbalance is the charge-balance error (CBE), and is used to verify the validity and quality of water analyses. The charge balance error of the water analysis was calculated using the formula below;

$$\boldsymbol{CBE} = \frac{\sum_{i=1}^{i}[\boldsymbol{cations}] - \sum_{i=1}^{i}[\boldsymbol{anions}]}{\sum_{i=1}^{i}[\boldsymbol{cations}] + \sum_{i=1}^{i}[\boldsymbol{anaions}]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(.)}$$

Where [ ] = concentration in milliequivalent (C_{meq}), defined as

$$\boldsymbol{C_{meq}} = \frac{\boldsymbol{concentration\ in\ mg/L}}{\boldsymbol{atomc\ weight}}\ \boldsymbol{x\ z} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(.)}$$

where z is the charge on the ion.

When CBE is positive, implies that one or more of the cations was over determined or one or more of the anions was under-determined, or both. On the other hand, a negative CBE indicates that one or more of the cations was under-determined, or one or more of the anions was over-determined, or both. In water analysis, CBE within ± 5% are acceptable water (Freeze and Cherry, 1979). The results of groundwater analyses in the study were accepted within ± 5 % (Appendix 2).

4.6 Calculation of Groundwater Quality Index (GWQI)

The water quality index (WQI) was determined for groundwater samples to ascertain its quality for domestic use. The parameters used for the calculation of the WQI included pH, EC, TDS, Na, K, Ca, Mg, F^-, Cl^-, HCO_3^-, NO_3^-, SO_4^{2-}, As, Cd, Fe, Ni and Pb.. The water quality index was calculated using the Arithmetic Weighted Method (AWM) using the Equation 4.18(Khwakaram *et al.*, 2012):

$$\boldsymbol{WQI} = \frac{\sum_{i=1}^{n} \boldsymbol{Q_i W_i}}{\sum_{i=1}^{n} \boldsymbol{W_i}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(.)}$$

Where Q_i is the quality rating of ith parameter for a total of n water quality parameters, and W_i is Relative weight for the nth parameter.

The quality rating (Q_i) and the relative weight (W_i) were obtained by applying equations (4.13) and (4.14) respectively.

$$Q_i = \frac{V_a - V_i}{S_i - V_i} x\, 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (.)$$

Where $\mathbf{V_a}$ is the actual value of the water quality parameter obtained from laboratory analysis$\mathbf{V_i}$ is the ideal value of that water quality parameter and $\mathbf{S_i}$isthestandard permissible value recommended by WHO. The ideal value for each parameter in this study was taken as zero except for F^- = 1 due to its importance in dentistry and pH = 7

The unit weight, $\mathbf{W_i}$for each parameter was calculated by a value inversely proportional to the standard permissible value, $\mathbf{S_i}$for each parameter and given as:

$$W_i = \frac{1}{S_i} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (.)$$

The WQI parameters, their standard values, ideal values assigned unit weight has been presented in Table ..

Table .: WQI parameters, their standard values, ideal values assigned unit weight(WHO, 2008; Khwakaram *et al.*, 2012)

Parameters	Standard permissible limit Value (Si)	Ideal Value (I)	Unit weight (Wi) = 1/Si
pH	8.5	7	0.118
EC	500	0	0.002
TDS	1000	0	0.001
HCO3	500	0	0.002
Ca	100	0	0.010
Mg	30	0	0.033
Na	200	0	0.005
K	10	0	0.100
F	1.5	1	0.667
Cl	250	0	0.004

Parameters	**Standard permissible limit Value (Si)**	**Ideal Value (I)**	**Unit weight (Wi) = 1/Si**
SO4	400	0	0.003
NO3	45	0	0.022
As	0.01	0	100.000
Cd	0.01	0	100.000
Fe	2	0	0.500
Ni	0.02	0	50.000
Pb	0.01	0	100.000

CHAPTER FIVE

RESULTS AND DISCUSSION

5.1: Results

5.1.1 Groundwater Recharge Estimation

5.1.1.1Water Balance method

Results for the estimation of surface runoff showed that, surface runoff occurred in the wet months of May to Septemberwhere there was appreciable rainfall.Surface runofffrom October to April where low rainfall is usually recorded was practically zero. Therefore mean annual surface runoff for the study area was calculated from mean monthly runoff for the wet months from May to September. The mean monthly surface runoff for the study area ranged from 8.52 to 126 mm with a mean of 52.59 mm (Table .). The mean daily evapotranspiration (ETo) ranged from 4.1 to 6.2 mm with an average of 5.2 mm. This translated into mean monthly ETo ranging from 124.14 to 191.15 mm with an average of 157.98 mm (Table .). Groundwater recharge estimated by the WBM (Table .) produced a recharge rate of 59.79 mm/year corresponding to 6% of mean annual rainfall for the study area.

Table .: Mean monthly surface runoff (Qs) for the study area with a catchment area of 286 km^2.

Month	**Qs (m^3)**	**Qs (mm)**
MAY	2.44×10^6	8.52
JUN	7.57×10^6	26.47
JUL	15.72×10^6	54.96
AUG	36.09×10^6	126.18
SEP	13.39×10^6	46.82
SUM	**75.02** $\times 10^6$	**262.95**
Mean	**15.04×10^6**	**52.59**
Max	**36.09×10^6**	**126.18**
Min	**2.44×10^6**	**8.52**

Table .: Mean daily and monthly ETo for Navongo, (estimated by using Cropwat 8.0 Beta based on Pennman-Monteith data).

Month	**Min Temp**	**Max Temp**	**Humidity**	**Wind**	**Sun**	**Rad**	**Daily ETo**	**Monthly ETo**
	°C	°C	%	m/s	hours	MJ/m²/day	mm/day	mm/month
January	20.2	35.5	26	1.8	8.8	20.1	5.7	177.86
February	22.9	38.0	24	1.7	8.6	21.2	6.2	172.44
March	25.8	39.7	33	1.5	7.7	21.0	6.2	191.15
April	26.7	39.0	51	1.6	7.9	21.7	6.2	185.95
May	25.5	36.3	63	1.5	8.3	21.9	5.7	175.52
June	23.9	33.3	73	1.4	7.8	20.8	4.9	146.24
July	23.0	31.5	78	1.2	7.0	19.7	4.3	134.49
August	22.7	30.8	82	1.7	6.0	18.5	4.1	126.33
September	22.6	31.6	80	0.9	6.8	19.6	4.1	124.14
October	22.7	34.5	71	1.0	8.1	20.7	4.6	142.00
November	20.6	37.1	46	1.2	9.3	21.0	5.1	152.46
December	19.5	35.9	31	1.6	9.1	20.0	5.4	167.17
Average	**23.0**	**35.3**	**55**	**1.4**	**8.0**	**20.5**	**5.2**	**157.98**
Max	**26.7**	**39.7**	**82**	**1.8**	**9.3**	**21.9**	**6.2**	**191.15**
Min	**19.5**	**30.8**	**24**	**0.9**	**6.0**	**18.5**	**4.1**	**124.14**

Table .: Results of groundwater recharge estimation by WBM

	(mm)	**% of P**
Mean Annual Rainfall (P)	996.74	100.00
Mean Surface Runoff (Q$_s$)	262.95	26.48
Mean Annual Evapotranspiration (ETo)	673.06	67.53
Mean Annual Recharge (R)	59.79	6.00

5.1.1.2 Chloride Mass Balance Method

The long term mean annual rainfall in Navrongo is 997 mm/year (Ghana Meteorological Agency (GMA), 2015). The Cl$^-$ concentration in rainwater had a mean of 0.65 mg/L and ranged from 0.20 mg/L to 1.40 mg/L (Appendix 3A) whiles the Cl$^-$ concentrations in groundwater ranged from 4.10 mg/L to 39.97 mg/L with an average concentration of 14.76 mg/L. The Cl$^-$ concentration factor (ratio of Cl$^-$ in groundwater to rainwater) ranged from 0.0163 to 0.1625 with a mean 0.0577 (Appendix 3B).

Thiscorrespondedtogroundwater recharge rate ranging from 16.2 to 158 mm/year with an average of 56.7 mm which representing a percentage recharge ranging from 1.6 to 16% with a mean of 5.7% of mean annual rainfall (Table .).(See sample calculation of CMB method in Appendix 3B).

Table .: Results of groundwater recharge by CMB method (Clp = 0.65, mean annual rainfall = 997 mm)

	Clgw (mg/L)	Clp/Clgw	Recharge mm/yr	% Recharge/yr
Mean	14.8	0.06	56.74	5.69
Max	40.0	0.16	158.02	15.85
Min	4.1	0.02	16.21	1.63

5.1.2 Hydrochemistry of Groundwater Samples

The physico-chemical parameters in the groundwater samples (Table .) generally showed a spatial variation in terms pH, TDS and EC among samples. Temperature however, did not vary much. The pH, ranged from 6.62 to 7.83, with a mean of 6.95. The TDS and EC values ranged from 148.00 to 397.00 mg/L and 220.90 to 592.50μS/cm with respective means of 271.84 mg/L and 405.70 µS/cm. Temperature ranged from 31.33 to 34.5℃ with an average of 32.33℃. The TDS of all groundwater samples had values less than 1000 mg/L. This suggested that they were all from freshwater sources (Freeze and Cherry, 1979). These values were comparable to those obtained by Martin(2006) in the Atankwidi Catchment but slightly higher than those obtained by (Barnie *et a*l., 2014). The concentrations of Na^+ and K^+ ranged from 30.4 to 74.6 mg/L and 0.5 to 7.4 mg/L with respective means of 51.1 and 3.5 mg/L (Table .).The levels of Ca^{2+} and Mg^{2+} also had means of 30.15 and 6.62 mg/L and ranged from 11.76 to 41.51 and 0.28 to 12.00 mg/L respectively.The levels of Cl^-, HCO_3^- and SO_4^{2-} ranged from 4.01 to 39.97, 98.51 to 320 and 1.77 to 16.77 mg/L, with means of 14.72, 228, 6.37 mg/L respectively (Table .).

Table .: Hydrochemistry of groundwater for the Atankwidi Catchment

Sample	pH	TDS	EC	Temp	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	F^-	NO_3	SO_4^{2-}
AK08	7.73	162	241.79	32.33	50.2	4.5	35.90	8.36	265.55	12.12	0.22	0.037	3.55
AK09	7.83	241	359.70	32.14	50.1	4.4	30.43	8.16	252.81	8.32	0.48	0.025	4.36
BAL01	6.96	167	249.25	31.56	45.0	3.1	27.80	7.12	198.23	7.99	1.09	0.017	10.65
BAL02	6.67	208	310.45	31.28	38.2	1.1	22.39	4.94	175.32	12.01	0.91	0.036	6.77
BAL03	6.83	161	240.30	31.19	40.0	1.2	22.22	3.60	154.19	12.00	0.37	0.066	6.13
KAN01	6.62	297	443.28	31.5	54.5	3.4	30.42	7.76	198.47	31.97	0.40	0.080	7.26
KAN03	6.89	305	455.22	32.22	70.1	3.2	29.54	7.50	276.99	23.98	0.34	0.120	13.71
KAN05	6.74	362	331.34	31.28	73.5	1.5	40.07	4.28	298.33	19.96	0.40	0.077	7.74
KAN07	7.01	165	291.04	31.67	35.3	0.6	12.92	1.16	98.51	23.95	0.43	0.079	7.10
KAN09	7.03	299	446.27	34.5	55.4	2.1	38.62	6.24	270.06	19.99	0.47	0.076	2.90
KAN12	6.98	397	368.66	33.28	45.1	4.7	32.44	8.56	198.07	23.89	0.40	0.068	5.00
KAN14	6.99	366	546.27	34.06	66.1	2.8	35.43	6.76	268.84	27.69	0.44	0.096	10.00
KAN16	6.88	272	405.97	33.78	48.1	4.5	28.41	8.46	260.06	8.10	0.37	0.088	9.03
NAG02	6.93	370	552.24	32.5	70.8	1.4	39.00	4.00	284.11	8.10	1.11	0.081	16.42
NAG03	6.99	161	265.67	34.39	50.0	3.1	30.14	6.24	238.68	19.79	0.69	0.020	3.07
NAG05	6.9	350	522.39	31.39	51.7	1.4	30.55	4.00	240.23	12.44	0.55	0.017	3.87
NAG07	6.88	276	337.31	32.39	62.7	4.1	32.01	8.12	288.34	8.12	0.46	0.021	4.84
NAG08	6.99	278	240.30	33.17	55.8	4.2	28.47	8.16	248.58	8.10	0.43	0.020	2.58
NAG09	7.05	356	531.34	32.5	56.0	4.3	31.75	8.10	265.56	12.00	0.71	0.040	6.13
NAG10	6.82	349	520.90	31.67	53.2	2.3	30.84	6.12	255.07	15.99	0.78	0.028	3.39
SOM05	6.87	369	550.75	31.33	74.6	5.3	40.05	8.20	320.08	8.00	1.69	0.830	2.26
SOM01	6.85	166	247.76	32.17	30.4	1.4	21.10	4.40	150.68	16.24	1.10	0.027	5.97
SOM02	6.81	148	205.97	32.5	38.7	5.7	16.65	1.64	125.19	12.00	0.71	0.054	9.19
SOM03	6.63	293	437.31	32.56	41.8	5.4	37.12	10.80	224.33	27.95	1.48	0.102	15.00
SOM04	6.82	225	335.82	31.78	50.2	2.8	25.05	6.02	232.78	8.00	1.69	0.111	16.77
SRI01	7.21	241	359.70	32.78	55.5	4.9	20.52	6.00	254.6	8.00	0.28	0.030	2.90
SRI03	6.76	361	538.81	33.28	47.4	6.0	39.71	11.88	258.47	19.99	0.24	0.055	6.77

Sample	**pH**	**TDS**	**EC**	**Temp**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-**	**Cl^-**	**F^-**	**NO_3**	**SO_4^{2-}**
SRI05	6.98	164	331.34	32.78	41.2	4.3	30.93	8.36	212.06	8.00	0.29	0.018	2.74
SRI07	7.25	166	243.28	32.21	53.3	1.2	18.73	0.28	144.68	19.99	0.39	0.026	4.36
SRI09	7.06	164	247.76	32.89	35.6	1.1	25.69	3.08	125.89	23.95	0.45	0.035	4.19
SRI11	7.08	163	282.09	31.56	34.7	4.9	32.86	7.96	190.19	15.91	0.30	0.021	2.42
SRI13	7.06	299	243.28	32.83	37.0	7.4	40.07	12.00	240.32	12.00	0.83	0.033	3.87
SRI15	7.25	265	395.52	32.5	49.7	3.1	30.11	8.04	205.45	19.97	1.05	0.073	5.00
SRI17	7.07	390	432.84	32.61	60.9	2.0	28.55	6.80	263.29	8.00	0.64	0.044	5.48
SRI19	7.2	344	513.43	32.44	53.6	1.7	40.84	3.92	268.78	4.10	1.39	0.030	4.52
YUA01	6.81	353	526.87	32.06	45.5	4.5	39.05	8.60	253.6	8.00	1.19	0.031	4.68
YUA03	6.96	241	359.70	31.89	41.0	4.3	30.89	8.76	188.93	19.29	0.81	0.039	7.10
YUA06	6.93	379	565.67	31.33	60.5	6.2	37.96	6.00	269.11	15.49	1.14	0.009	1.77
YUA07	7.03	345	514.93	31.89	51.8	6.5	41.51	10.60	284.23	8.00	0.88	0.032	4.68
YUA08	7.13	274	408.96	31.61	47.5	3.5	31.04	8.40	235.07	4.10	0.36	0.044	6.13
YUA09	7.14	375	559.70	31.5	68.6	1.8	26.50	6.80	268.48	8.00	0.66	0.025	4.19
ZOK001	6.66	167	244.78	32.61	47.6	0.5	24.09	4.40	178.66	12.11	0.90	0.050	10.81
ZOK03	6.68	269	401.49	32.11	37.7	5.0	30.12	6.84	225.34	8.10	0.65	0.017	3.87
ZOK05	6.77	282	420.90	32.83	50.5	7.0	29.35	7.72	198.52	39.97	1.23	0.037	6.94
ZOK07	6.76	313	467.16	32.33	66.7	4.4	28.53	6.16	259.45	8.31	0.75	0.096	11.13
ZOK09	6.71	286	426.87	32.67	64.7	1.4	24.05	4.40	255.73	15.91	0.60	0.019	3.39
ZOK10	6.79	275	410.45	31.89	57.2	2.4	29.10	7.64	243.95	8.20	0.48	0.055	8.39
ZOK12	6.74	274	408.96	32.61	43.0	5.7	31.33	9.12	224.93	16.11	1.66	0.031	7.10
ZOK15	6.98	295	440.30	32.06	43.5	5.2	34.80	7.12	228.16	12.13	1.05	0.022	4.19
ZOK16	6.77	164	249.25	31.94	54.2	2.6	11.76	1.36	141.43	23.59	1.43	0.042	8.07
Mean	**6.95**	**271.84**	**388.63**	**32.33**	**51.1**	**3.5**	**30.15**	**6.62**	**228.17**	**14.72**	**0.75**	**0.063**	**6.37**
Max	**7.83**	**397**	**565.67**	**34.50**	**74.6**	**7.4**	**41.51**	**12.00**	**320.08**	**39.97**	**1.69**	**0.830**	**16.77**
Min	**6.62**	**148**	**205.97**	**31.19**	**30.4**	**0.5**	**11.76**	**0.28**	**98.51**	**4.10**	**0.22**	**0.009**	**1.77**

5.1.3. Trace Elements in Groundwater

Trace elements levels in groundwater in this work were generally low with most having concentrations below detection limit. Concentration of As, Cd, and Co ranged from <0.001 to 0.007 mg/L, <0.002 to 0.008 mg/L and <0.005 to 00.036 mg/L respectively with means of 0.007, 0.003 and 0.027 mg/L.The levels of Fe and Mn ranged from <0.006 to 0.644 mg/L and <0.002 to 0.104 mg/L with corresponding averages of 0.234 and 0.036 mg/L whereas Ni and Pb ranged from <0.010 to 0.092 mg/L and <0.001 to 0.014 mg/L with means 0.062 and 0.007 mg/L respectively (Table .). Copper, chromium and zinc generally had concentrations below detection limit.

Table .: Trace elements concentration (mg/L) in groundwater from the study area

Sample	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
AK08	<0.001	0.001	<0.005	<0.006	<0.003	0.304	<0.002	<0.010	<0.001	<0.001
AK09	0.002	0.002	<0.005	<0.006	<0.003	0.188	<0.002	0.056	<0.001	<0.001
BAL01	<0.001	<0.002	<0.005	<0.006	<0.003	0.06	<0.002	<0.010	0.008	<0.001
BAL02	0.016	<0.002	<0.005	<0.006	<0.003	0.302	0.02	<0.010	0.012	<0.001
BAL03	0.012	<0.002	<0.005	<0.006	<0.003	0.316	<0.002	<0.010	0.003	<0.001
KAN01	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	<0.001	<0.001
KAN03	0.003	0.006	0.028	<0.006	<0.003	<0.006	<0.002	0.084	0.005	<0.001
KAN05	0.012	0.002	<0.005	<0.006	<0.003	0.452	<0.002	<0.010	<0.001	<0.001
KAN07	0.003	0.007	0.024	<0.006	<0.003	<0.006	<0.002	<0.010	0.013	<0.001
KAN09	0.012	0.002	0.028	<0.006	<0.003	<0.006	<0.002	0.044	0.008	<0.001
KAN12	<0.001	0.002	<0.005	<0.006	<0.003	0.0196	0.068	<0.010	<0.001	<0.001
KA14	0.002	0.002	<0.005	<0.006	<0.003	<0.006	0.024	<0.010	<0.001	<0.001
KAN16	<0.001	0.008	<0.005	<0.006	<0.003	0.156	<0.002	<0.010	<0.001	0.02
NAG02	<0.001	0.004	0.028	<0.006	<0.003	<0.006	<0.002	0.040	0.007	<0.001
NAG03	0.002	<0.002	<0.005	<0.006	<0.003	0.044	0.012	<0.010	<0.001	<0.001
NAG05	0.002	0.003	<0.005	<0.006	<0.003	0.124	<0.002	0.062	<0.001	<0.001
NAG07	0.002	0.002	0.02	<0.006	<0.003	<0.006	<0.002	<0.010	0.010	<0.001
NAG08	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	<0.001	<0.001
NAG09	0.002	0.002	<0.005	<0.006	<0.003	<0.006	<0.002	0.082	0.007	<0.001
NAG10	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	<0.001	<0.001

Sample	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
S0M05	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.01	<0.020	<0.001
SOM01	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	<0.001	<0.001
SOM02	<0.001	0.003	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	0.003	<<0.001
SOM03	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	<0.001	<0.001
SOM04	<0.001	<0.002	<0.005	<0.006	<0.003	0.22	<0.002	0.092	<0.001	<0.001
SRI01	0.002	<0.002	0.024	<0.006	<0.003	0.644	<0.002	0.08	<0.001	<0.001
SRI03	0.002	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	0.052	<0.001	<0.001
SRI05	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	0.024	<0.010	0.008	<0.001
SRI07	<0.001	0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	0.012	<0.010
SRI09	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	0.003	<0.001
SRI11	0.010	0.002	0.036	<0.006	<0.003	<0.006	<0.002	0.072	0.009	<0.001
SRI13	0.008	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	0.014	<0.001
SRI15	0.010	<0.002	<0.005	<0.006	<0.003	0.364	<0.002	<0.010	<0.001	<0.001
SRI17	0.001	0.004	0.036	<0.006	<0.003	0.036	<0.002	0.06	0.011	<0.001
SRI19	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	<0.001	0.001
YUA01	<0.001	0.003	<0.005	<0.006	<0.003	0.196	<0.002	<0.010	<0.001	0.008
YUA03	0.001	0.002	0.024	<0.006	<0.003	0.38	0.104	0.052	<0.001	<0.001
YUA06	0.012	0.002	<0.005	<0.006	<0.003	0.152	<0.002	<0.010	<0.001	<0.001
YUA07	<0.001	<0.002	0.024	<0.006	<0.003	<0.006	<0.002	0.052	<0.001	<0.001
YUA08	0.002	<0.002	<0.005	<0.006	<0.003	0.112	0.02	<0.010	<0.001	<0.001
YUA09	0.002	<0.002	<0.032	<0.006	<0.003	0.54	0.052	0.06	<0.001	<0.001
ZOK01	<0.001	0.002	0.024	<0.006	<0.003	0.052	<0.002	<0.010	0.002	<0.001
ZOK03	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	<0.001	<0.001
ZOK05	0.002	<0.002	0.032	<0.006	<0.003	<0.006	<0.002	0.056	0.007	<0.001
ZOK07	<0.001	<0.002	<0.005	<0.006	<0.003	0.252	0.02	<0.010	0.002	<0.001
ZOK09	<0.001	<0.002	0.024	<0.006	<0.003	<0.006	<0.002	<0.010	0.004	<0.001
ZOK10	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	0.012	<0.01	0.011	<0.001
ZOK12	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	<0.001	<0.001
ZOK15	<0.001	<0.002	<0.005	<0.006	<0.003	<0.006	<0.002	<0.010	0.004	<0.001
ZOK16	0.002	0.004	0.032	<0.006	<0.003	<0.006	<0.002	0.044	0.008	<0.001
Average	**0.007**	**0.003**	**0.027**	**<0.006**	**<0.003**	**0.234**	**0.036**	**0.062**	**0.007**	**0.01**
Max	**0.010**	**0.008**	**0.036**	**<0.006**	**<0.003**	**0.644**	**0.104**	**0.092**	**0.014**	**0.020**
Min	**<0.001**	**<0.002**	**<0.005**	**<0.006**	**<0.003**	**<0.006**	**<0.002**	**<0.010**	**<0.001**	**<0.001**

5.2 Discussion of Results

5.2.1 Groundwater Recharge

5.2.1.1 Water Balance Method (WBM)

Recharge by the Water Balance Method (WBM) was estimated using Equation 4.4. Results for the estimated parameters of the WBM have been summarised inTable .. All meteorological data used for WBM were from 1983 to 2015 except for rainfall which were from 1961 to 2015. The largest fraction of the water balance was evapotranspiration (ETo) and ranged from 4.1 to 6.2 mm/day with an average of 5.2 mm/day (Table .).The highest ETo was observed in March whereas the least occurred in September.The month of March is characterised by high daily temperatures ranging fromabout 25 to40℃ coupled with low humidity of about 33%. This might have accounted for the high ETo while the low ETo observed in September was explained by the low daily temperatures ranging from about 23 to 32℃ and the high humidity of about 80%.Recharge to groundwater depends on amount of precipitation (P), evapotranspiration (ETo) and surface runoff (Qs) and occurs when P >ETo + Qs. Recharge therefore is likely to occur in the wet months from June to October. Evapotranspiration for these months were therefore used to estimate recharge.The total annual ETo was 673 mm and accounted for 67.53% of the long-term mean annual rainfall. The estimated surface runoff was 263 mm representing 26.48% of the long-term mean annual rainfall. The long term mean annual rainfall in Navrongo is 997 mm (GMA, 2015).By applying Equation 4.4, the groundwater recharge by WBM yielded 59.79 mm/annum which amounted to 6% of mean annual rainfall (Table .). This value was less than that (13%) obtained by (Martin, 2006)for the year 2003 but slightly higher than the 4% obtained for 2004 for the same study area using soil moisture balance method. The difference observed could beattributed to the differences in methods.Also, inaccuracies in the measurementand estimation of climatic and hydrological parameters such as evapotranspirationand surface runoff could be responsible for the difference.

5.2.1.2 Chloride Mass Balance (CMB) Method

The chloride concentration factor was used to determine the rate of groundwater recharge. This factor is the ratio of chloride concentration in rainwater (Cl_p) to the chloride concentration in groundwater (Cl_{gw}). The Cl^- factor is used to calculate how much of precipitation has actually been evaporated (Ritort, 2007). The distribution of recharge rates based on Chloride mass-balance (CMB) was calculated using Equation 4.7 for each sample point. The validity of the groundwater recharge estimation by CMB method was based on the assumption that precipitation was the only source of chloride in groundwater and that, chloride is conservative ion. Although, weathering/dissolution of basement or aquifer materials, seawater intrusion and anthropogenic activities could significantly affect the chloride level in groundwater, these were neglected in this study due to the following reasons:

(i). The geology of the study area is a weathered granitoid zone (Matin, 2006) where halite has not been known to be a major mineral. Hence the contribution of Cl^- from the dissolution of halite is insignificant. This point was supported by the Na+/Cl- ratio greater than 1 (Appendix 4)

(ii). The study area is located very far from the sea hence intrusion by seawater is negligible

(iii). Also survey conducted in the study revealed that there is no industrial or any anthropogenic activity in the area which could possibly introduce significant amount of Cl^- into the groundwater. The major land use activity in the study area is rain fed farming with minimal traditional irrigation farming and

(iv). The TDS in all the groundwater samples were less than 1000 mg/L and suggested that they were fresh and quite recent(Freeze and Cherry, 1979).This implied that they had less contact time with aquifer minerals and as a result has not undergone pronounced rock-water interaction. The groundwater therefore has not dissolved many substances to significantly affect the Cl^- level.

Based on these analogies, the assumption that precipitation is the only source of chloride to the groundwater is valid.

The groundwater recharge in the Atankwidi catchment estimated using CMB method ranged from 16.2 mm/year to 158 mm/year with mean of 56.7 mm/year giving rise to percentage recharge ranging from 1.6% to 15.9% with mean of 5.7% (Table .).The variation in the groundwater recharge rate at the various sample locations in the study area could be attributed to local factors such as the differences in the local vegetation within the area, which affects the amount of evapotranspiration that could occur, the thickness of the vadose zone and thus the amount of water that can evapotranspire from the top of water table as well as the depth of the water table at each sample point. Recharge rate by CMB method was similar to earlier value of 6% of mean annual rainfall reported by Martin (2006) for the Atankwidi Catchment but less than that (9.0% of mean annual rainfall) obtained by Afrifa (2003) in Gushegu, in the Northern Region of Ghana which is also within the White Volta Catchment but to the south of the study area. Pelig-Ba (2000) obtained 4.5% of annual recharge for Tamale in the Northern Region of Ghana also within theWhite Volta River Basin using CMB method which was lower than that obtained in this study.The results of recharge by

CMB also showed that about 935 mm (94%) of rainfall is lost through evapotranspiration and runoff annually. This value was in line with those obtained by the Water Resource Commission of Ghana in Tamale (913 mm/year), Yendi (910 mm/year), Bole (908 mm/year)(IWRM, 2008) andGushegu (911 mm/year) (Afrifa, 2013) all in the Northern Region and within the White Volta River Basin.

5.2.1.3 Comparison of Recharge between WBM and CMB Methods

The rate of recharge by WBM and CMB method were similar. The WBM recharge rate was 6% whiles that of the CMB was 5.7%. Both methods showed that an average of about 94% of mean annual rainfall is lost through evapotranspiration and surface runoff. The WBM showed that evapotranspiration contributed to about 68% and about 26% for surface runoff. The rate of recharge obtained in this work was within the range of 2 to 13% obtained by Martin (2006). Generally, much of the water lost from rainfall is through evapotranspiration and it is explained by the high daily temperatures and sometimes high winds in the study area.

5.2.2 Major Ion Chemistry of Groundwater and Mineralisation Processes

Dissolved ions constitute by far the greater part of TDS in groundwater. The release of dissolved ions into groundwater may depend on several factors including their relative solubilities, reaction kinetics of the minerals, pH and temperature (Adomako, 2010). The concentrations of dissolved ions in groundwater is determined by the hydrogeochemical processes that take place within the aquifer system (Lakshmanan *et al*., 2003). These processes occur when the groundwater moves towards equilibrium in major ion concentration. Hence, the source(s) of dissolved ions as well as the processes that lead to their release into groundwater could be predicted by the type and amount of the various chemical species present and their interrelationships

(Appelo and Postma, 1996; Lakshmanan *et al*., 2003). Mineral solubility is greatly influenced by the action of CO_2 produced within the soil zone by root respiration, bacterial metabolism on the solid mineral phases within the soil and decomposition of organic matter (Appelo and Postma, 1996; Anku *et al*., 2008).

The major ion composition of groundwater in this study showed wide variations among cations and anions. The order of dominance of cations was $Na^{+} > Ca^{2+} > Mg^{2+} > K^{+}$ and $HCO_3^{-} > Cl^{-} > SO_4^{2-}$, NO_3^{-} for anions.

Excess calcium and magnesium in groundwater may originate from the dissolution of various minerals such as dolomite, gypsum, calcite, anhydrite or weathering of silicate minerals such as plagioclase, pyroxene, amphibolites and montmorillonite(Garrels, 1976; Freeze and Cherry, 1979; Boghici and Van Broekhoven, 2001).Datta and Tyagi (1996) showed that in (Ca^{2+} + Mg^{2+}) against (HCO_3^{-} + SO_4^{2-}) bi-plot, ionic concentrations that fall above the 1:1 line indicates carbonates weathering whereas those falling below indicate silicate weathering. Those that fall along the 1:1 equiline also result from both carbonate and silicate weathering. The plot of Ca^{2+} + Mg^{2+} versus HCO_3^{-} + SO_4^{2-} in this study (Figure .) showed that, all the points fell below the 1:1 equiline. This suggested that, the main source of Ca^{2+} and Mg^{2+} in groundwater from the study area came from silicate weathering.

The contribution of cations to groundwater by silicate weathering can also be predicted by the (Na^{+} + K^{+})/total cations (TZ^{+}) index as cited in (Lakshmanan *et al*., 2003). Datta and Tyagi (1996) reported that contribution of cations may be derived from silicate weathering when (Na^{+} + K^{+}) = $0.5TZ^{+}$). In the present study, it was observed from the plot of (Na^{+} + K^{+}) against (TZ^{+}) (Figure .) that all the point clustered around the (Na^{+} + K^{+}) = $0.5TZ^{+}$ which was typical for cation contribution from silicates (Lakshmanan *et al*., 2003).

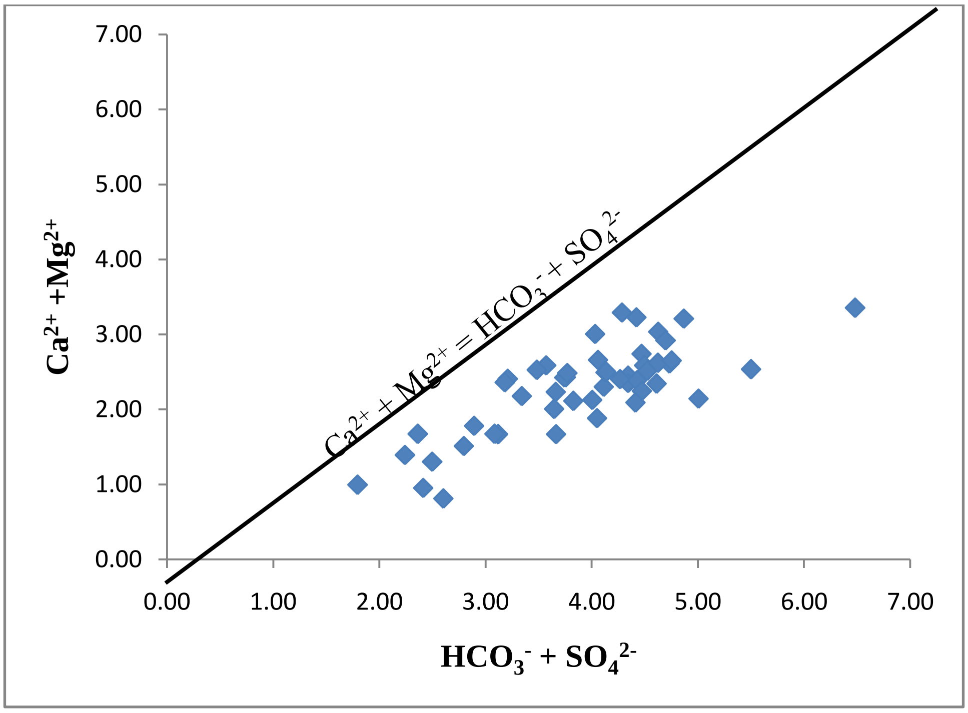


Figure .: Scatter diagram of Ca^{2+} + Mg versus HCO_3^- + SO_4^{2-}

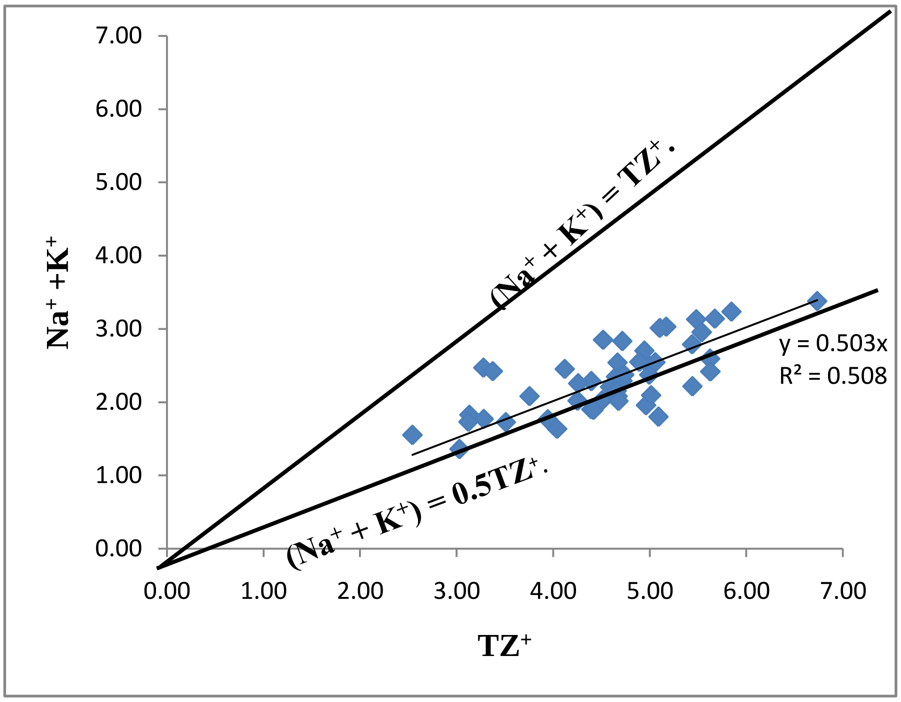


Figure .: Plot of Total cations (TZ^+) versus Na^+ + K^+ in groundwater in the study area

Sodium ion was the dominant cation in groundwater in the study area whiles K^+ was the least. The presence of Na^+ and K^+ in groundwater in this study could be attributed to weathering of alkali silicates such as plagioclase, K-feldspar, biotite and muscovite. The weathering of silicate minerals such as K-feldspar and plagioclase (albite) is caused by the action of carbonic acid (H_2CO_3). The H_2CO_3 is formed from the reaction between atmospheric carbon dioxide (CO_2) and water (H_2O) according to Equation 5.2. The resulting H_2CO_3 then reacts with silicates in the soil according to Equation 5.3 and 5.4 leading to release of Na^+, K^+, HCO_3^- and other associated ions that may be present into groundwater (Faure, 1998; Lakshmanan *et al.*, 2003)

$CO_2 + H_2O \rightarrow H_2CO_3$………………………………………………………… **(.)**

$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 4H_4SiO_4 + 2HCO_3^-$.. **(.)**

$2KAlSi_3O_8 + 9H_2O + H_2CO_3 \rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 4H_4SiO_4 + 2HCO_3^-$…… **(.)**

Therefore, the extreme increased levels of Na^+ over K^+observed suggested that albite dissolution was probably the major contributor of Na^+ in the groundwater.

In addition to that, all the groundwater samples, had $Na+/[Na^+ + Cl^-]$ ratio > 0.5 (Appendix 3) which may indicate sodium sources are mainly from cation exchange and incongruent dissolution of alumino-silicate (Na-plagioclase or albite) (Adomako *et al.*, 2010). Also plot of $Ca^{2+} + Mg^{2+}$ versus total cations (TZ^+) (Figure .) showed that all samples lie far below the 1:1 equiline depicting the contribution of alkalis to the major ions.

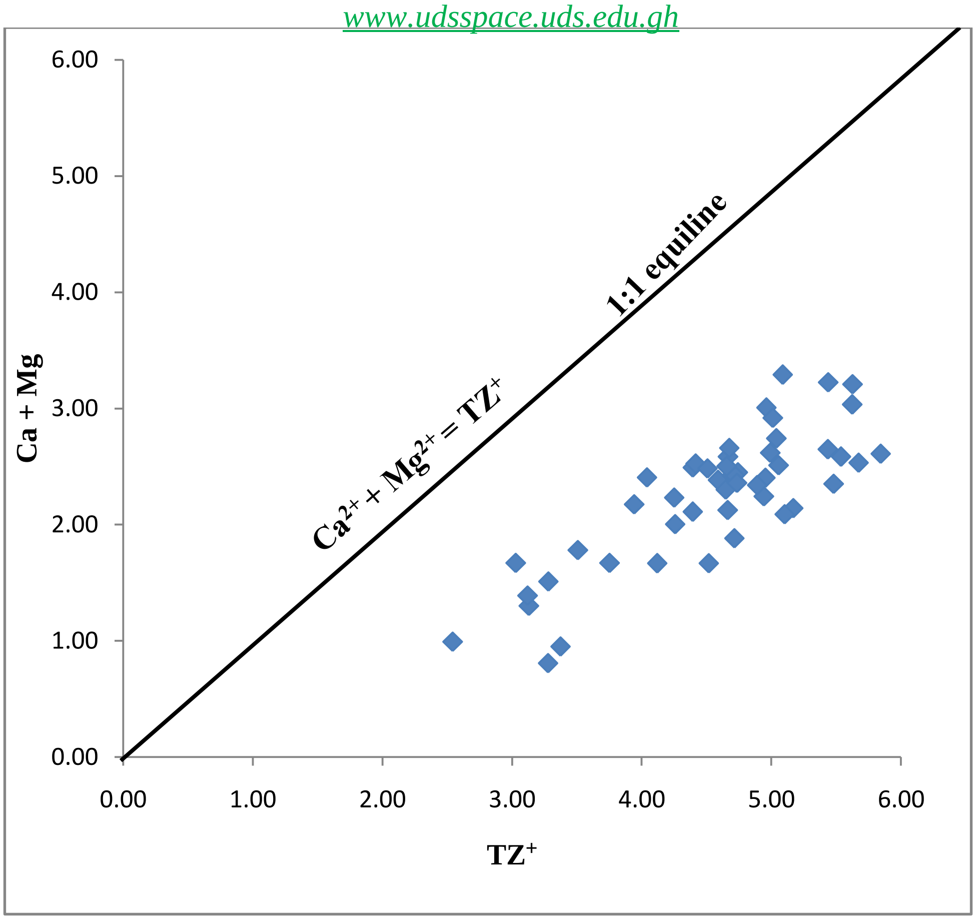


Figure .: Plot of Ca+Mg against Total cations

Furthermore, elevated levels of Na^+ in groundwater could also result from seawater intrusion, halite (NaCl) dissolution, evaporation or ion exchange process. However, the possibility of the Na^+ from seawater intrusion in the study was ruled out due to the location of the study area which is far from the coast. Also, the geology of the study area is underlain by crystalline rocks with low permeability or porosity hence seepage of seawater is negligible. Hounslow, (1995)reported that groundwater derived from seawater intrusion will have $Na^+/(Na^+ + Cl^-)$ ratio less than 0.5 and Cl/ total anion (TZ^-) greater than 0.8. The $Na^+/(Na^+ + Cl^-)$ and Cl/TZ^- ratios in groundwater from the study area were all greater that 0.5 and less than 0.8 respectively (Appendix 3). This confirmed that, Na^+ in groundwater was derived from sources other thanseawater intrusion. Again, halite dissolution or evaporation would leave Na^+/Cl^- ratio of 1:1.

Therefore, a plot of Na^+ against Cl^- would fall along the 1:1 equiline whiles a plot of Na^+/Cl^- versus EC would produce a horizontal line (Senthilkumar and Elango, 2013). Such plots (Figure . and Figure .) showed that all plotted points were above the 1:1equiline in Na^+ against Cl^- scatter diagram whereas that of Na^+/Cl^- against EC also produced an inclined line. This suggested no halite dissolution or evaporation process in the study area. This provided further evidence to support the fact that the source of Na^+ was probably derived from silicate weathering or cation exchange.

Meybeck (1987) reported $Na^+/Cl^- > 1$ to be typical for Na^+ released from silicate weathering. The Na/Cl ratio >1 (Appendix 3) therefore further supported the release of Na^+ from sources other than halite dissolution.

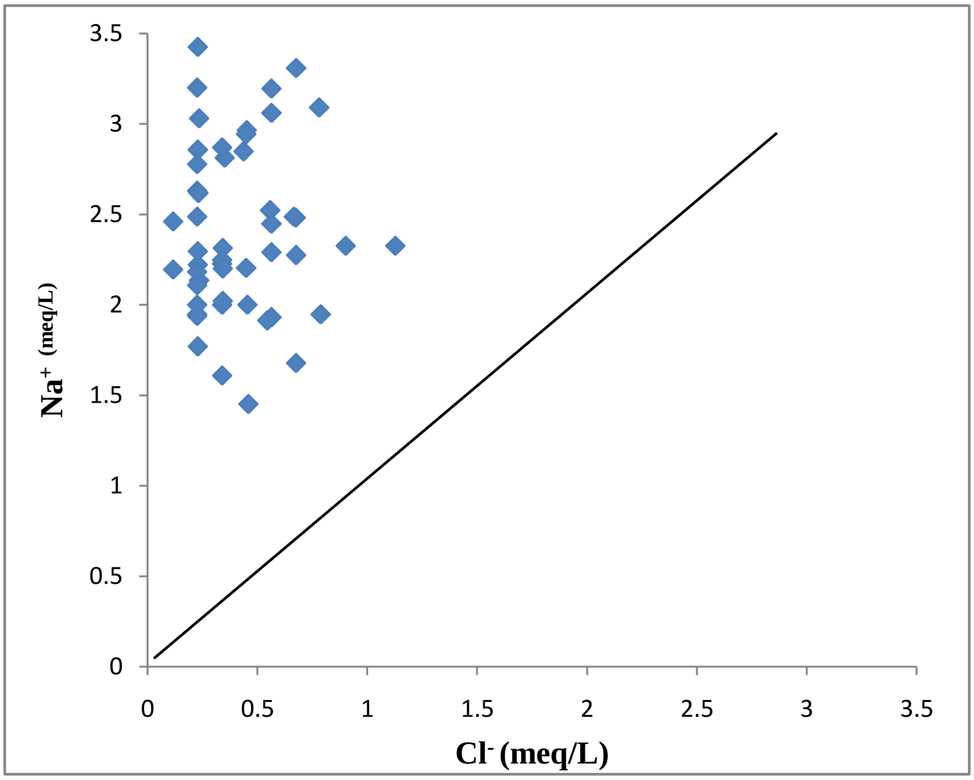


Figure .: Plot of Na^+ against Cl^-

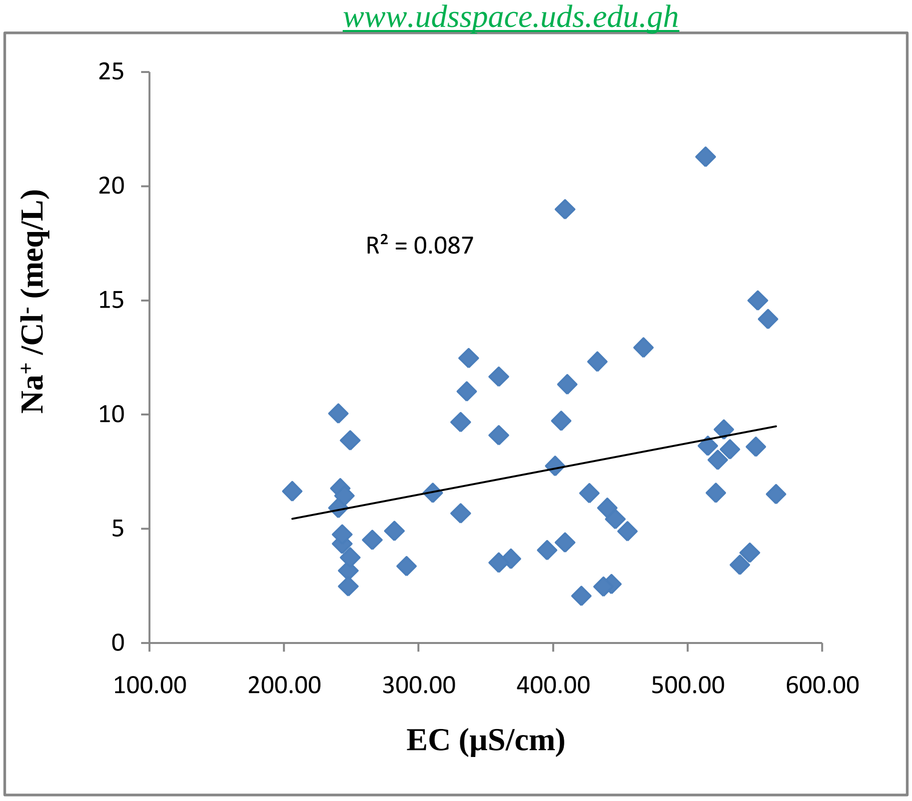


Figure .: Plot of Na^+/Cl^- against EC

The plot of TZ^+ against HCO_3(Figure .) showed that incongruent dissolution of silicates might have contributed significantly to concentration of Ca^{2+} and Mg^{2+}.

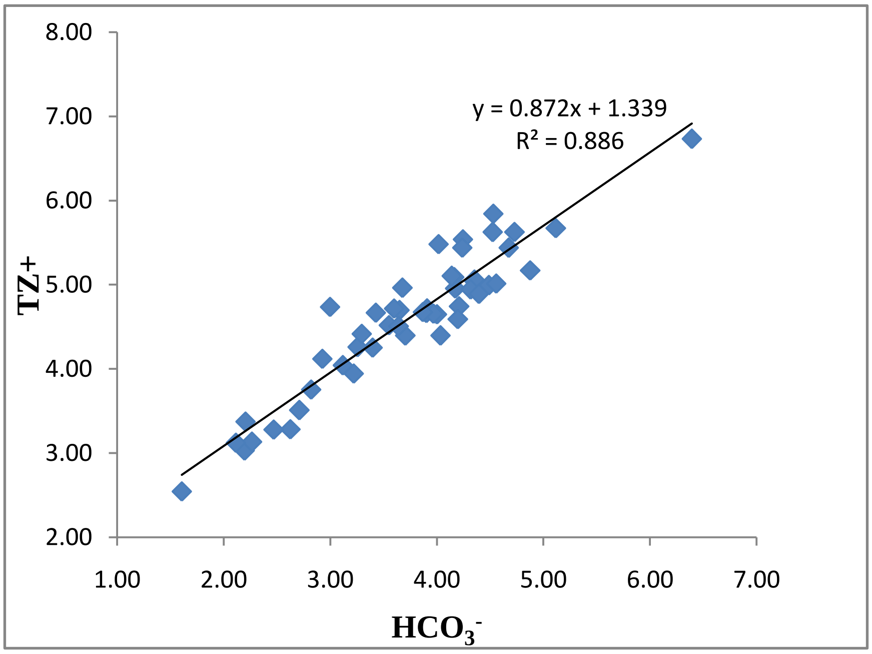


Figure .: Plot of total cation versus HCO_3^-

Lakshmanan *et al.*, (2003) reported that high Na^+ over Ca^{2+} in groundwater could be attributed to ion exchange processes. Plot of Na^+ against Ca^{2+} (Figure .) showed increased levels of Na^+ with respect to Ca^{2+} and suggested Na/Ca ion exchange. That is, Na^+ might have replaced Ca^{2+} in cation exchange process.Schoeller, (1965) used chloro-alkali indices 1 and 2 ($CA1$ and $CA2$) given by Equation 5.4 and 5.5 to study the ion exchange between groundwater and its host environment.

$$\boldsymbol{CA1 = \frac{Cl^- - (Na^+ + K^+)}{Cl^-}} \text{..}\textbf{(.)}$$

$$\boldsymbol{CA2 = \frac{Cl^- - (Na^+ + K^+)}{SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-}} \text{...}\textbf{(.)}$$

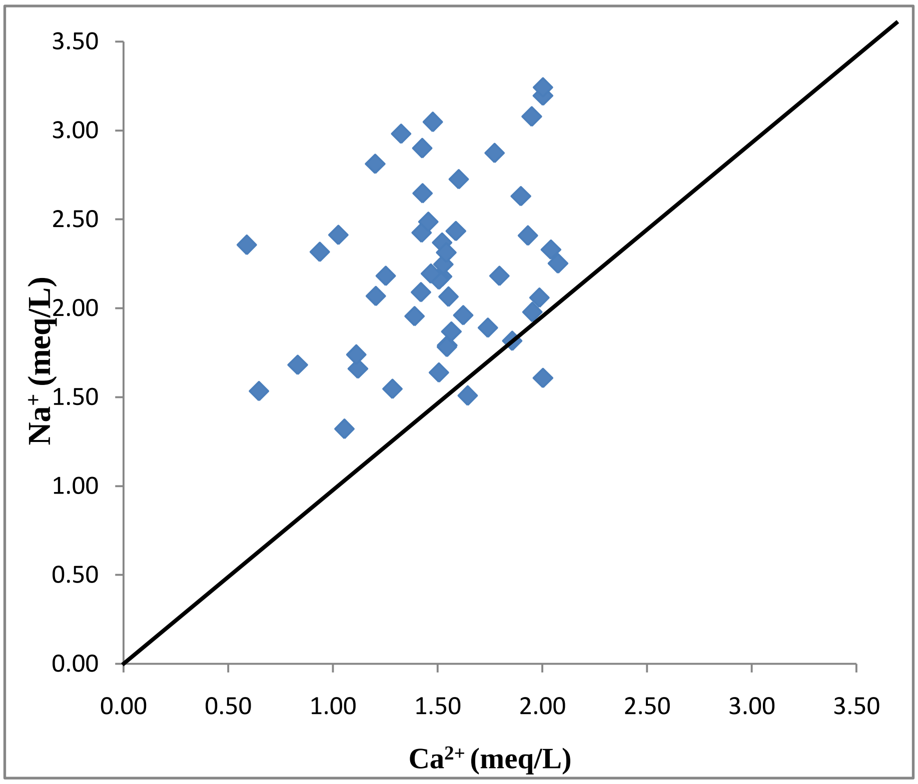


Figure .: Plot of Na^+ against Ca^{2+}

Schoeller, (1965) showed that when there is an exchange between Ca^{2+} or Mg^{2+} in the groundwater with Na^+ and K^+ in the aquifer material, both indices are negative, and if there is a reverse ion exchange, then both of these indices will be positive.The chloro-alkali indices calculated for groundwater samples in the study area were all negative (Appendix 3) and suggested ion exchange reaction mainly the exchange between Ca^{2+} or Mg^{2+} in the groundwater with Na^{+} and K^{+} in the aquifer material.

In another study, Jankowski *et al.*, (1998) used a bivariate plot of $[(Ca^{2+} + Mg^{2+}) - (HCO_3^{-} + SO_4^{2-})]$ as a function of $(Na^{+} - Cl^{-})$ (Figure .) where all the constituents were expressed in meq/L and explained that waters undergoing cation exchange would plot along a line whose slope is -1 while water samples plotting close to the zero value on the x-axis would not be influenced by cation exchange.

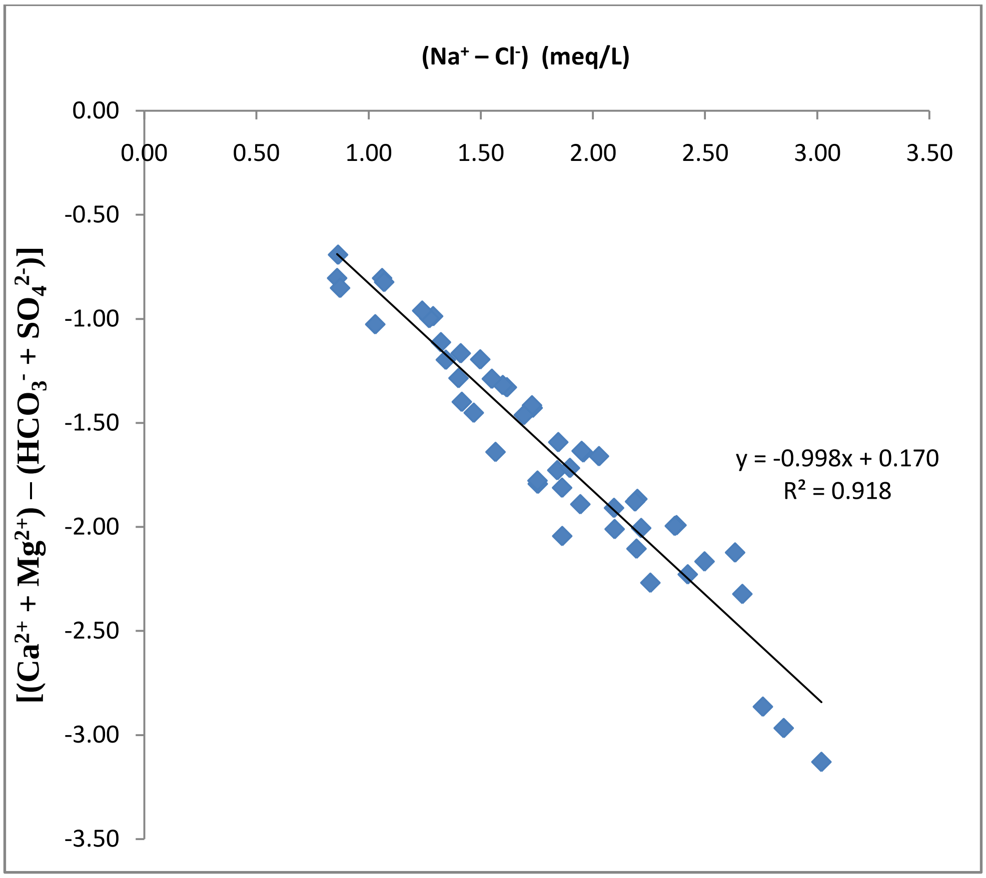


Figure .: Plot of $[(Ca^{2+}+Mg^{2+}) - (HCO_3^{-} + SO_4^{2-})]$ versus $(Na^{+} - Cl^{-})$

From Figure .it was observed that all the samples plotted away from the x-axis but clustered around the trend line with gradient of -0.998 (R^2 = 0.9189) suggesting that Ca^{2+}, Mg^{2+}, Na^+ and K^+ participate in ion exchange reaction.

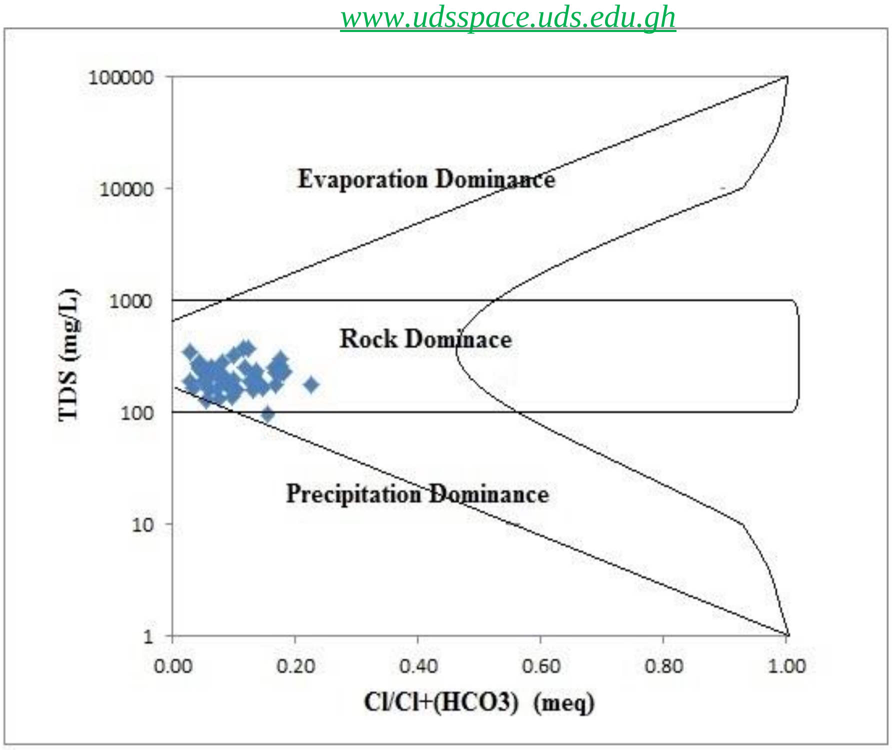
The presence of NO_3^- in groundwater is generally from NO_3^- sources on land surface or subsurface (soil zone) or in shallow subsoil zones where nitrates-rich substances are buried (Freeze and Cherry, 1979). Sources of NO_3^- on land surface come from the application of fertilisers and other nitrate waste. Nitrate may also find its way into groundwater through the conversion of organic nitrogen (NH_4^-) or ammonium (NH_4^+) to nitrates (Freeze and Cherry, 1979).Generally, NO^{3-} ions concentrations in excess of 5 mg/L have been reported to be associated to pollution by human and animal waste, or fertiliser run-off (Chapman and Kimstash, 1996).The low levels of NO_3^- in groundwater in this study therefore suggested little pollution to the aquifer.

Common sources of Cl^- in groundwater could arise from atmospheric deposition or dry fallout which gets dissolved in recharging water. Chloride in groundwater could also come from weathering and dissolution of halite or saline water intrusion. However, the contribution of Cl^- in groundwater by saline water intrusion and halite dissolution in the study area were ruled out based on the location of study area and the Na^+/Cl^- ratio (Figure .(a)). The Cl^- in the groundwater was therefore attributed to meteoric Cl^- dissolved in recharging water. Dominance of HCO_3^- in groundwater was attributed to silicate weathering in the presence of dissolved CO_2 as illustrated by Equations 5.1, 5.2, and 5.3.

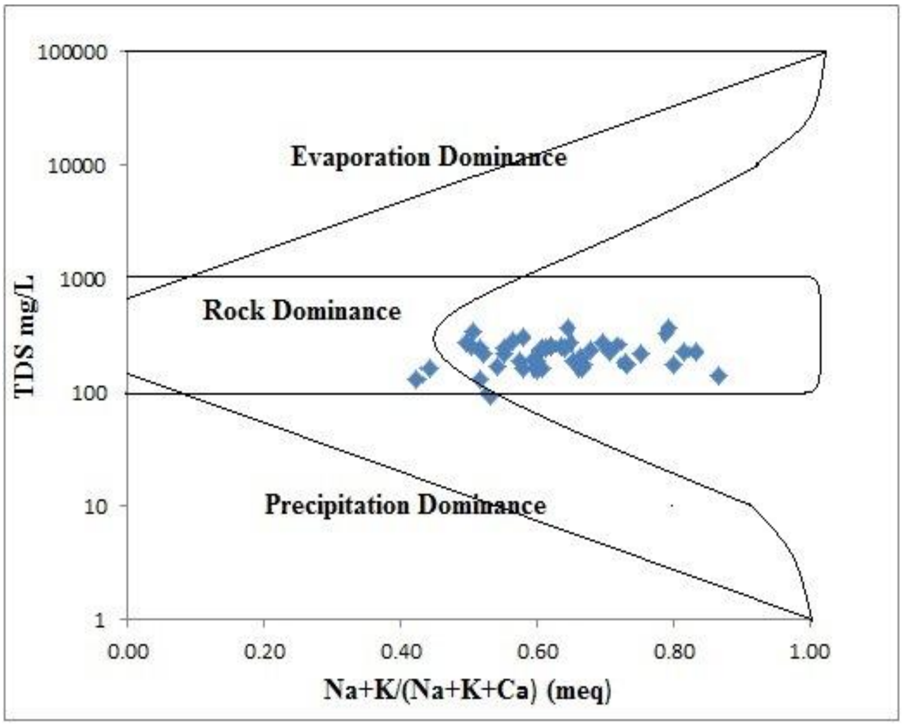
Sulphates in groundwater may originate from natural and anthropogenic sources. Sulphates (SO_4^{2-}) has been reported to arise from the atmospheric deposition of oceanic aerosols and the leaching of sulphur compounds, either sulphate minerals such as gypsum or sulphide minerals such as pyrite, epsomite, mirabillite, from sedimentary rocks (Appelo and Postma, 1996). The main occupation of the study area is rain-fed farming along side small scale irrigation where organic and inorganic fertilisers are applied to boost productivity. The sulphate levels in the groundwater could be attributed partly to anthropogenic activities through the continuous application of fertilisers in the study area.

5.2.3 Mechanisms Controlling Groundwater Chemistry

The mechanism controlling water chemistry and the functional sources of dissolved ions can be assessed by plotting the ratios of Cl^- to (Cl^- + HCO_3^-) and Na^+ to (Na^+ + Ca^{2+}) as functions of TDS (Gibbs plot) (Figure .,Gibbs, 1970). The Gibbs plot has three distinct regions (Precipitation dominance, Rock dominance and Evaporative crystallation or simply evaporation dominance) which define the source of dissolved ions and mechanism(s) responsible for the water chemistry in a particular area. From the Gibbs plot, (Figure .(a) and (b)) it was observed that all the samples plotted in the rock dominance region which suggested that the groundwater chemistry in the study area was mainly controlled by the geology of the area Thus, chemical weathering of rocks minerals (rock water interaction) was the main process controlling water chemistry in the Atankwidi Catchment. This was in line with the bi-plots of (Ca^{2+} + Mg^{2+}) against (HCO_3^- + SO_4^{2-}) (Figure .) which suggested silicate weathering (rock water interaction) was the major contributor of dissolved ions in groundwater. It was also in support of the fact that, there was no saline water intrusion or evaporation processes in (Figure . and Figure .).



a)



b)

Figure .: Gibbs diagrams for groundwater samples from the study area

5.2.4 Statistical Anaylyses

The R statistical software version 3.2.3 (2015-12-10) for windows was used to perform principal component, and hierarchical cluster analysis to support the conventional hydrochemical techniques. The *FactoMineR* package version 1.28 developed by Francois Husson, Julie Josse, Sebastien Le, and Jeremy Mazet, for Multivariate Exploratory Data Analysis and Data Mining with R, was used to perform principal component analysis and Hierarchical clustering on the principal components (Lê *et al*., 2008). The Ward's method of Hierarchical clustering was used. Prior to clustering analysis, principal component analysis was performed on the hydrochemical dataset of groundwater samples using the PCA function of the package. The number of component retained were the principal components whose eigenvalues were above one (Husson *et al*., 2011).

a) Principal Component Analysis (PCA)

Principal component analysis (PCA) was performed on twelvehydrochemical variables (EC, TDS, pH, temperature, Na^+ , K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}). Prior to PCA the dataset was log-transformed and standardized according to Equation 5.6.

$$\boldsymbol{z_{i,j} = \frac{d_{i,j} - \overline{d_i}}{s_i}} \text{……………………………………………………………………}\textbf{(.)}$$

Where; $\overline{d_i}$ and s_i are the mean and standard deviation of all $d_{i,j}$ $j = 1, n$. With this transformation, the mean of each transformed variable is zero and standard deviation is 1 (Drever, 1982). In this study, four (4) principal components (PC) explained about 63.29% of variance of the dataset (Table .).

Component 1 explained **32.90**% of the total variance (Table .) and was strongly correlated by HCO_3^-, EC, TDS, Ca^{2+}, Mg^{2+} and Na^+ (Table .). The strong correlation of these hydrochemical parameters to this component suggested some higher degree of water-rock interaction mainly dissolution of silicate minerals in rocks and soil constituents.

Table .: Eigenvalues and the percentage of total varimax explained by PCA based on varimax matrix

Principal Component	Eigenvalue	Percentage Of Variance	Cumulative Percentage Of Variance
1	**3.95**	**32.90**	**32.90**
2	**2.12**	**17.66**	**50.56**
3	**1.53**	**12.73**	**63.29**
4	0.99	8.28	71.57
5	0.88	7.31	78.89
6	0.72	6.03	84.91
7	0.53	4.45	89.36
8	0.47	3.89	93.25
9	0.36	3.00	96.25
10	0.30	2.47	98.73
11	0.13	1.08	99.81
12	0.02	0.19	100.00

Principal component 2 was strongly and positively correlated by SO_4^{2-} and NO_3^- whereas it was strongly and negatively correlated by K^+ and pH.This component accounted for **17.66**% of the total variance. The negative correlation of K^+ and pH with SO_4^{2-} and NO_3^-suggested that they did not come from the same source. Component 2 could be attributed to the anthropogenic activities through the application of organic and inorganic fertilisers.

Component 3 explained **12.73**% of the total variance and was moderately and positively correlated by Cl^-, temperature K^+, and Mg^{2+}. This suggested that Cl^-, K^+ and Mg^{2+} were probably derived from the same source. This component was attributed to the dissolution of biotite associated with the geology.

Table .: Correlation of the five PC loadings

Component 1	Correlation	p.value
HCO$_3^-$	0.95	6.44e-26
TDS.	0.87	4.17e-16
EC.	0.82	4.40e-13
Ca^{2+}	0.82	5.24e-13
Na$^+$	0.62	1.27e-06
Mg^{2+}	0.55	3.04e-03

Component 2	Correlation	p.value
SO$_4^{2-}$	0.69	2.83e-08
NO$_3^-$	0.54	4.86e-05
K$^+$	-0.54	5.62e-05
pH	-0.63	1.20e-06

Component 3	Correlation	p.value
Cl$^-$	0.52	9.1e-05
Temp	0.56	1.30e-04
K$^+$	0.51	1.83e-04
Mg^{2+}	0.53	2.16e-05

b) Cluster Analysis (CA)

The main motive of doing CA was to classify the sampling sites based on their spatial similarities. Hierarchical Cluster Analysis (HCA) was performed in R-mode and Q-mode, the Wards method was applied and Euclidean metric was used as a measure of similarity. The cluster revealed two distinct groups or clusters (Figure .).The different clusters and their members were extracted as follows for the R-mode HCA: cluster one included HCO$_3^-$, TDS, EC, Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$and temperature while cluster two includedCl$^-$, NO$_3^-$, SO$_4^{2-}$pH. Parameters within the same cluster suggested that they were related, perhaps they originated from the same source or their release into groundwater were affected by similar conditions.The clusters of the physicochemical parameters in this study (Figure .) suggested that major mineralisation processes were from rock water interaction probably silicate weathering. This supported the principal component analysis. Cluster one was attributed to weathering of rock minerals whereas cluster two was attributed anthropogenic activities

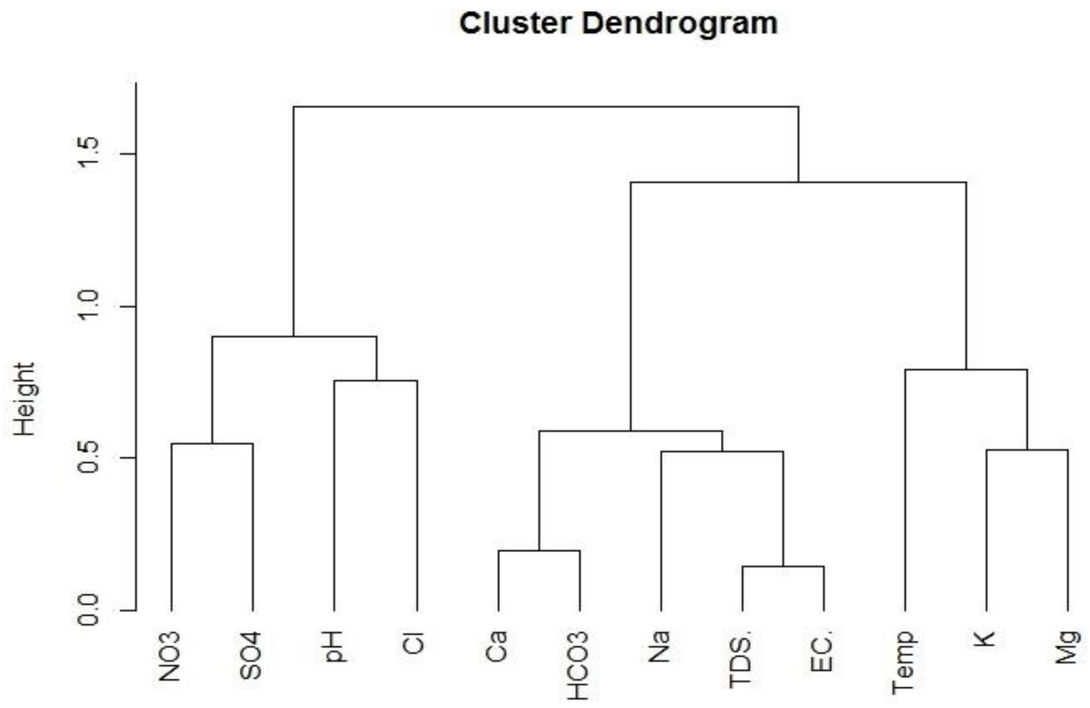


Figure .: Dendrogram of 12 physicochemical parameters in groundwater from the study area

Hierarchical Cluster analysis (HCA) onhydrochemistry of groundwater has been presented in dendrogram (Figure .).The HCA classified 50 sampling points into three major groups. The mean and standard deviation of the hydrochemistry of the groups have been presented inTable .andthe physical significance of the results was tested by relating the statistically defined clusters with their geographical locations.The most distinguishing factor among the groups seemed to be the TDS with concentration of major ions increasing in the order: Group 1 < Group 2 < Group 3 except for Cl^- and SO_4^{2-} which was in the order Group 2 < Group 3 < group 1.

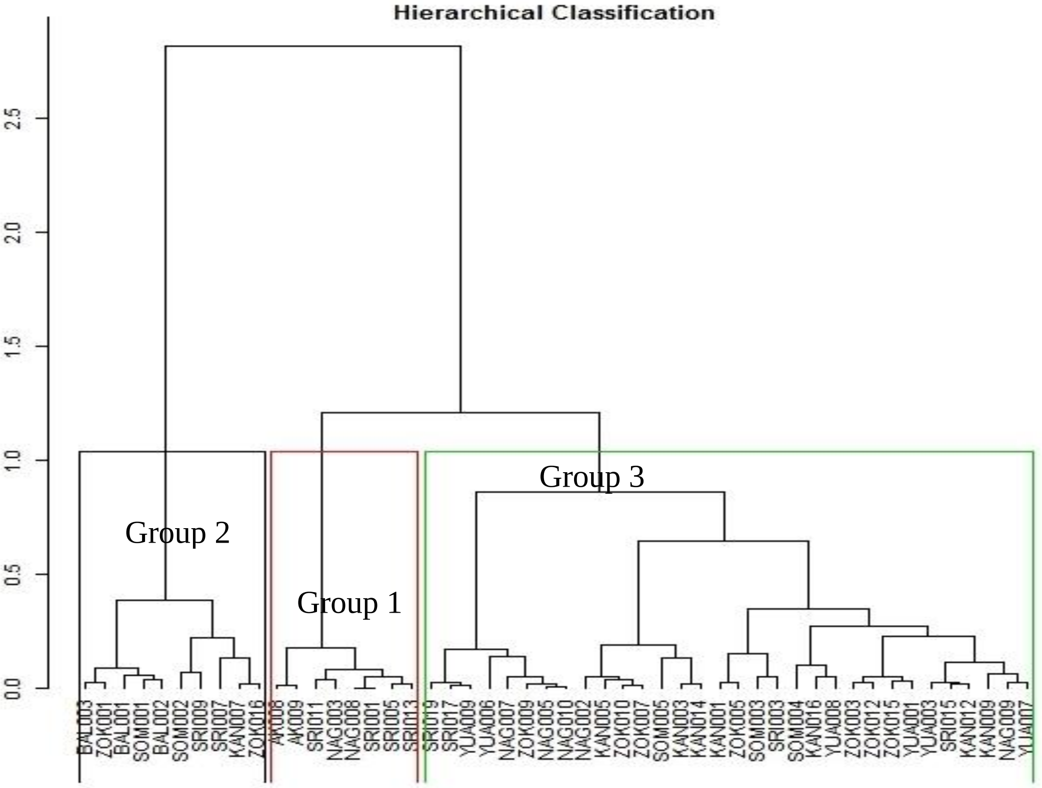


Figure .: Dendrogram of Hierarchical clustering on first principal component

Table . Summary of physicochemical composition for the four groups of groundwater in the study area defined by HCA (all parameters are in mg/L except for EC ($\mu S/cm$) and pH)

Parameters	Group 1 n = 10		Group 2 n=8		Group 3, n=32	
	Mean	±SD	Mean	±SD	Mean	±SD
pH	6.89	0.18	7.23	0.35	6.90	0.16
TDS	167.60	15.27	213.63	57.81	318.97	47.41
EC	252.99	28.61	290.49	52.17	455.55	72.36
Temp	31.83	0.58	32.64	0.88	32.02	1.15
Cl^-	16.38	6.02	11.53	4.39	15.00	8.72
Na^+	41.83	7.93	46.81	8.13	55.11	10.27
K^+	3.00	2.38	3.88	1.37	3.97	1.75
Ca^{2+}	17.14	6.45	30.54	5.74	32.18	6.11
Mg^{2+}	6.90	2.63	10.81	1.05	11.19	3.31
NO_3^-	0.04	0.02	0.03	0.01	0.08	0.14
HCO_3^-	148.89	29.58	240.98	24.38	249.38	42.43
SO_4^{2-}	9.32	2.34	5.19	0.68	8.86	3.96

5.2.5 Hydrochemicalfacies and Groundwater Classification

Hydrochemicalfacies are distinct zones that have cation and anion concentration categories. Piper trilinear plot developed by Piper (1944) was used to study the chemistry and classification of groundwater with respect to major cations and anions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^- and SO_4^{2-}.In the cations plot of the Piper diagram (Figure .)about 50% of the samples plotted in the middle of the triangle. This indicated mixed type cations with no dominant cation exceeding 50% in those samples. The other 50% plotted in the region of Na + K which indicated the predominance of the alkalis (Na^+ and K^+) over the alkali earths in those samples. In the anions plot all the samples plotted in the region of $HCO_3^- + CO_3^{2-}$ which indicated that the predominant anion was HCO_3^-. This distribution of cation and anions gave rise to three main water types namely mixed Na-Ca-HCO_3, Na-Ca-Mg-HCO_3 and Na-HCO_3, water types.This suggested that the groundwater samples were quite recent and regarded as recharge water at its early stage of evolution (Freeze and Cherry, 1979).This implied that, the groundwater has not undergone pronounced rock-water interactions. This was in line with TDS levels < 1000 mg/L (Table .) in groundwater which indicated they were from fresh water sources.

5.2.6 Groundwater Quality for Domestic Use

5.2.6.1 Trace Elements Concentrations in Groundwater

Trace elements are classified into essential, non-essential and toxic elements and their occurrence in the environment may be through natural and anthropogenic sources (Arhin *etal*., 2015). Essential trace elements such as Fe, Cu, and Zn are those that are required by the plants and/or animals in optimal amounts for their proper functioning whereas the non-essential ones include those that have no health benefits.

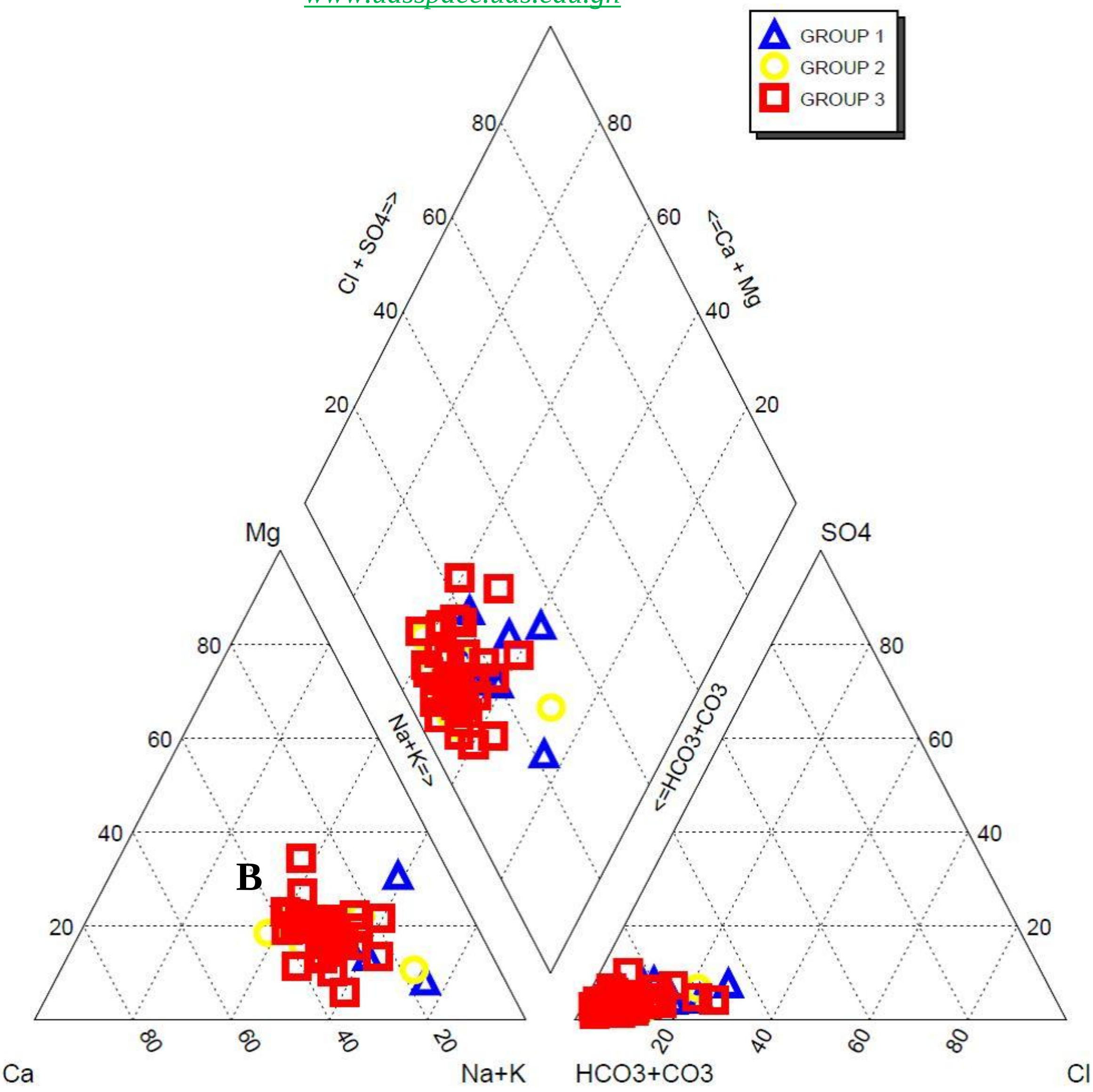


Figure .: Piper diagram of groundwater samples obtained from the Atankwidi Catchment area

Trace elements that are harmful to plants and animal life constitute the toxic trace elements and include Pb, Cd and As.

Trace elements occurrence in food and drinking-water is of outmost importance because at certain level even essential trace elements could have detrimental health effects. The quality of water suitable for domestic use particularly for human consumption is defined by the World Health Organisation (WHO). Hence, the concentrationsof trace elements in groundwater from the study area were compared with the guideline values set by WHO (2008)(Table .) to ascertain the suitability of the groundwater for drinking.

Table .: Summary of trace elements (mg/L) analysis in groundwater from the study area

Trace element	Min	Max	Mean	WHO Standard (2008)
As	<0.001	0.016	0.007	0.01
Cd	<0.002	0.008	0.003	0.01
Co	<0.005	0.036	0.027	-
Cr	<0.006	<0.006	<0.006	0.05
Cu	<0.003	<0.003	<0.003	1.3
Fe	<0.006	0.644	0.233	1
Mn	<0.002	0.104	0.036	0.05-0.5
Ni	<0.010	0.092	0.062	0.02
Pb	<0.001	0.014	0.007	0.01
Zn	<0.001	0.020	0.010	3.0

a) Arsenic (As)

Arsenic is widely found in the earth's crust in -3, 0, +3 and +5 oxidation states usually as sulphides, metal arsenides or arsenates with the arsenate (+5) form occurring mostly in water (WHO, 2008). Arsenic in natural waters occurs at low concentrations of less than 1-2 µg/L however, can have elevated levels particularly in groundwater in areas where there is sulphide mineral and sedimentary deposits derived from volcanic rocks (WHO, 2008). Arsenic has no known nutritional benefit in humans and is very toxic in the arsine form followed by arsenide and the organoarsenic compounds (WHO, 2008). Chronic signs of arsenicism include dermal lessions such as hypo- and hyperpigmentation, peripheral neuropathy, skin cancer, cancer of the bladder and lungs and peripheral vascular disease (WHO, 2008). The concentration limit of 0.01

mg/L of As is recommended in drinking-water (WHO, 2008). The range of As concentration in water obtained in groundwater from the Atankwidi Basin ranged from <0.001 to 0.016 mg/L with mean of 0.007 mg/L (Table .)and showed that 90% of the sample were within the recommended limit whereas 10% were slightly above the recommended level.

b) Cadmium (Cd)

Cadmium may be released into the environment in wastewater and diffuse pollution as a result of contamination from fertilisers and local air pollution (WHO, 2008). Nutritional benefit of Cd has not yet been reported (WHO, 1996; 2008). Cadmium primary bioacumulates in the kidney and is the main organ target for Cd toxicity (WHO, 2008). High Cd levels causes renal tubular dysfunction and subsequent pathological changes (Nogawa *et al.*, 1979). The guideline value for Cd in drinking-water is 0.003 mg/L (WHO, 2008). The Cd level in groundwater from the study area ranged from <0.002 to0.008 mg/L with mean of 0.003 (Table .). This showed that 90% of the samples were within the recommended limit whiles 10% of samples showed elevated levels above the guideline value and suggested a potential risk of Cd toxicity.

c) Cobalt (Co)

Cobalt often occurs in the earth crust in association with Ni, Ag, Pb, Cu and Fe ores in the form of arsenides, sulphides, oxides, such as linnaeite (Co_3S_4), carrolite ($CuCo_2S_4$), safflorite ($CoAs_2$), skutterudite ($CoAs_3$), erythrite ($Co_3(AsO_4)_2.8H2O$), and glaucodot (CoAsS) (Smith and Carson, 1981). Occurrence of Co in the environment is through natural and anthropogenic sources. The natural sources of Co include volcanic eruptions, seawater spray and forest fires whereas coal-fired power plants, incinerators and exhaust from vehicles constitute the anthropogenic sources. Other human induced sources of Co in the environment include Co mining and processing activities, the production of alloys and chemicals containing cobalt, sewage effluents, urban run-off, as well as agricultural run-offs and are known to be the major anthropogenic contributors of Co to the water bodies (Nagpal, 2004). Cobalt often occurs in the +2 and +3 oxidation states. However, the +3 state is thermodynamically unstable under the redox and pH conditions that commonly occur in natural waters with the exception of some complexes (Nagpal, 2004). Excessive oral exposure to Co has been liked to gastrointestinal effects, diarrhoea, liver injury and allergic dermatitis (Agency for Toxic and Substances and Disease Registry (ATSDR, 1992)). The guideline value for Co in dinking-water was not found in literature. Nagpal (2004) also reported the non-existence of guideline value for Co in water due to lack of data.

d) Chromium (Cr)

Chromium is found widely distributed in the earth’s crust and can exist in +2 to +6 oxidation states. The major sources of Cr in humans come from food with little contribution from water. No health-based based tolerable limit is set for Cr due to uncertainties in the toxicological database (WHO, 2008). However, Cr concentration of 0.05 mg/L is considered unlikely to give rise to significant health risks hence retained as provisional guideline value (WHO, 2008). Concentration levels of <0.006 mg/L (Table .)of Cr were obtained for groundwater samples from the study area hence were within the provisional guideline value.

e) Copper (Cu)

Copper is an essential trace nutrient and also a common contaminant in drinking-water (WHO, 2008). The main source of Cu in drinking water often comes from corrosion of interior Cu plumbing. It has also been reported that, Cu levels in fully-flushed or running water tend to be low and vice-versa (WHO, 2008). Many proteins found in humans such as superoxide dismutase, ceruloplasmin, cytochrome oxidase and others depend on Cu. Toxicity of Cu in infants is associated with liver dysfunction. The guideline value for Cu in drinking-water is 2 mg/L (WHO, 2008). The level of Cu in groundwater samples in this work were <0.003 (Table .)and therefore were well within the recommended limit.

f) Iron (Fe)

Iron is one of the most abundant in the earth crust and in the human body as far as essential trace elements are concerned (Huang and Failla, 2000; WHO, 2008). Iron levels ranging from 0.5 to 50 mg/L has been reported to be typical for natural fresh waters and may find it way into groundwater through the dissolution of rock minerals (WHO, 2008). Iron forms an important component of hemoglobin in humans and as such its deficiency could impair its functions. Irreversible alterations of brain functions and defects in immune response have been associated with low levels of Fe in humans (Beard, 2001). No guideline value is proposed for Fe in drinking-water. However, concentrations above 2 mg/L may affect the taste and appearance of drinking (WHO, 2008).Hence, WHO, (2008) allowable limit of Fe in water is 2 mg/L based on taste and appearance. The level of Fe in groundwater samples ranged from <0.006 to 0.644 mg/L (Table .) and were wellwithin the allowable limit.

g) Manganese (Mn)

Manganese often occurs with Fe and is one of the most abundant metals in the earth's crust. It is an essential element for humans and animals and naturally occurs in surface and groundwater particularly in low oxidation conditions (WHO, 2008). Manganese plays important role in growth, skeleton formation and reproductive functions (Wang *et al*., 2008). Manganese intoxication is associated with Parkinsonism which usually becomes progressive and irreversible and lead to the permanent damage of neurologic structures(Wang *et al*., 2008). Manganese deficiency is characterised by impaired growth, skeletal abnormalities depressed reproductive functions and ataxia in newborns (Wang and Du, 2008). Guideline value of 0.4 mg/L for Mn in drinking-water is recommended (WHO, 2008). The measured concentrations of Mn in groundwater in this study ranged from <0.002 to 0.104 mg/L (Table .) and were therefore within the recommended limit.

h) Lead (Pb)

Lead (Pb) is toxic element whose exposure causes several health problems particularly in infants. No health benefit of Pb has been reported (WHO, 1996). Increased blood pressure in adults has been linked to elevated body burden of Pb. Acute exposure to Pb causes renal tubular dysfunction in children. Other toxicological effects of Pb are usually associated with overt central nervous system effect and irreversible chronic intestinal nephropathy (WHO, 1996). Severe Pb toxicity leads to sterility, abortion, and neonatal mortality and morbidity (WHO, 1996). Guideline value for Pb in potable water is 0.01 mg/L. Analyses of groundwater samples in this work showed that the Pb concentration ranged from <0.001 to 0.014 mg/L (Table .) From these results, it was observed that forty-five samples representing 90%had Pb concentrations within the permissible limit whiles five samples amounting to 10% showed slightly elevated levels above the WHO, (2008) guideline value.

i) Nickel (Ni)

Exposure to Ni through water is minimal compared with food sources in non-smoking and non-occupationally exposed population. Nickel concentrations in drinking-water may be significant though in special cases of release from natural or industrial nickel deposits in the ground (WHO, 2008). Elevated levels of Ni in groundwater may largely be due to pollution. Metallic Ni has been reported to be a possible carcinogenic element however there is lack of evidence of risk from oral exposure to Ni (WHO, 2008). The maximum allowable limit of Ni in portable water is 0.07 mg/L. The amount of Ni in groundwater samples analysed from the study area ranged from <0.001 to 0.062 (Table .)thus within the recommended limit.

j) Zinc (Zn)

Zinc is an essential trace element present in virtually all food in the form of salts and organic complexes (WHO, 2008) It has several health benefits by acting as anti-inflamatory, antioxidant and borne resorptive. Deficiency of Zn in humans is characterized by growth failure, impaired parturition, neuropathy, hair loss and hypothermia (Moser-Veillon, 1990). The allowable limit of Zn in drinking-water is 3 mg/L. The concentration of Zn in groundwater from the Atankwidi Catchment ranged from <0.001 to 0.02 (Table .). These values were within the allowable limits therefore groundwater in study area is safe for drinking.

In general, the trace elements concentrations in groundwater from the study area were within the WHO (2008) guidelines for drinking-water with few isolated cases of slightlyelevated level of As, Cd and Pb.

5.2.6.2 Groundwater Quality Index (GWQI)

Groundwater quality index (GWQI) was assessed based on seventeen different parameters. These parameters included pH, EC, TDS, Na, K, Ca, Mg, Cl^-, F^-, HCO_3^-, NO_3^-, SO_4^{2-}, As, Cd, Fe, Ni and Pb. In this study, the GWQI was calculated for each sample based on the arithmetic weighted method explained in Section 4.6. Sample calculation has been presented in Appendix 5B. The results obtained showed that, the GWQI ranged from 0.06 to 68.09 with mean of 19.93(Appendix5A). This translated into water quality rating ranging from Excellent to Bad and for drinking. Sixtypercent (60%)of the groundwater samplehad WQI < 25 andsuggested they were excellent whereas 32% were found to be good for drinking with WQI between 25 and 50(Table .).Six percent(6%) of the samples had WQI between 50 and 75which suggested that they were poor whiles 2%had WQI between 75 and 100and were classified as bad for drinking (Table .).

Table .: Summary of waterquality index score for groundwater samples from the study area.

WQI SCORE (%)	QUALITY INTERPRETATION	NO. SAMPLES	% SAMPLES
0-25	Excellent	30	60
26-50	Good	16	32
51-75	Poor	3	6
76-100	Very poor (bad) water	1	2
>100	Unsuitable for drinking	Nil	Nil

5.2.7 Groundwater Quality for irrigation Use

5.2.7.1 Salinity Hazard

Salinity hazard is a measure of the TDS expressed in the unit of specific electrical conductance.It is the most influential parameter as far as the study of water quality for irrigation is concerned (Bauder *et al.*, 2007; Kortatsi *et al.*, 2009).High EC and for that matter high salinity in irrigation water impedes the proper functioning of crops through osmotic effect. High salinity affects the ability of crops to compete with ions in the soil for water thereby affecting crop yield. The severity of osmotic effect may vary depending on the plants age and could be unrecognised due to a uniform reduction of yield over the whole crop(Saleh*et al.*, 1999). Results obtained in this study revealed that the samples ranged from excellent to good for irrigation in terms of salinity. Eleven(11) samples (22%) were excellent whiles 39 samples (78%) were classified as good based on the criteria as described by Bauder *et al.*, (2007). This was in line with earlier report by (Barnie *et al.*, 2014)for this particular study area. Further details on the result of SH have been given in Table ..

Table .: Classification of groundwater samples in Atankwidi catchment for irrigation based on EC

No. of Samples	% Sample	EC (µS/cm)	Class of Water for Irrigation
11	22	≤250	Excellent
39	78	250 – 700	Good
0	0	750 – 2000	Permissible
0	0	2000 – 3000	Doubtful
0	0	≥3000	Unsuitable

5.2.7.2 Sodium Hazard (Sodium Adsorption Ratio)

Sodium adsorption Ratio (SAR) measures the relative concentration of Na^+ to Ca^{2+} + Mg^{2+} in a given water sample and is defined by Equation 5.7:

$$SAR = \frac{Na^{+}}{\sqrt{[(Ca^{2+}+Mg^{2+})/2]}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(.)}$$

where all units are expressed in meq/L (Tank and Chandel, 2010). The level of Na^{+} in irrigation water is essential as increased level makes it unsuitable for soils which contain exchangeable Ca^{2+} and Mg^{2+} ions as the soil tends to take up Na^{+} in exchange for Ca^{2+} and Mg^{2+} ions which results the dispersion of soils thereby affecting the soil texture and structure (Barnie *et al*., 2014). The SAR of groundwater samples obtained in this study were generally very low and ranged from 1.23 to 3.64 with an average of 2.14 (Appendix 4). All the samples fell within the acceptable limit (SAR>10) and thus were suitable for irrigation. Furthermore, Wilcox plot developed by Wilcox and Durum(1967)was used to determine the suitability of the groundwater samples for irrigation by plotting SAR as function of salinity (EC). The Wilcox plot (Figure .) in this study showed that, 18% of the samples plotted in the C1S1 field which indicated low SH and low alkalinity hazard. This suggested that those samples are excellent for irrigation on wide range of soils without fear of SH or exchangeable sodium. The rest of the samples plotted in the C2S1 field indicating medium SH and medium alkalinity hazard class of water hence good for irrigation on almost all types of soils with very little danger of SH or alkalinity hazard. Thus overall, all the groundwater samples from the study area is suitable for irrigation ranging from good to excellent based on SAR.

5.2.7.3: Sodium Percentage

Sodium content in water is a very essential factor in identifying its quality or suitability for irrigation because very high Na concentration can significantly affect soil permeability and structure which can be detrimental to crops growth (Jeyaseelan *et al*., 2013). The level of Na is usually quantified in terms of sodium percentage (%Na) defined by the Equation 5.8:

$$\%\boldsymbol{Na} = \frac{\boldsymbol{Na^{+}+K^{+}}}{\boldsymbol{Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}}}\ \boldsymbol{x\ 100}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\textbf{(.)}$$

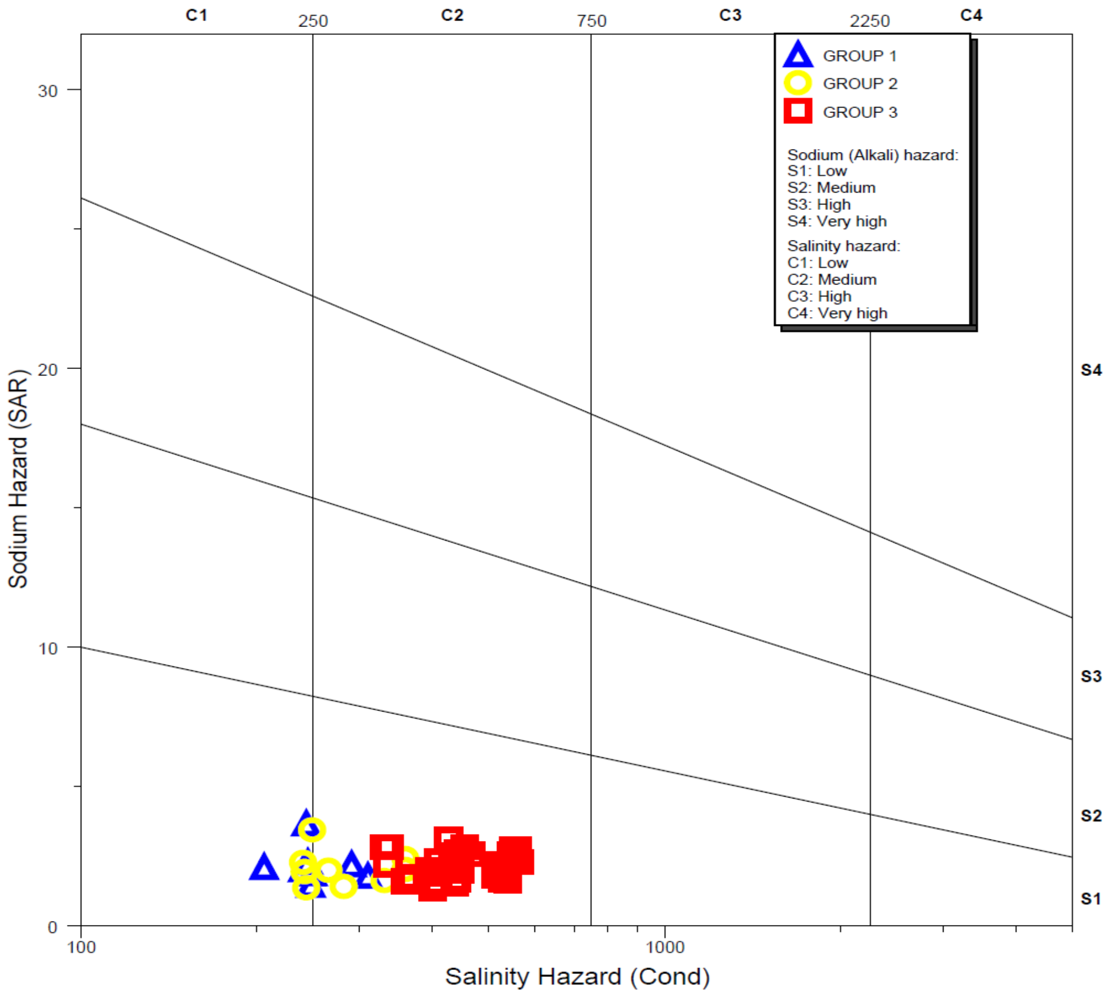


Figure .: Wilcox diagram for classification of groundwater for irrigation

Sodium percentage of less than 60% in groundwater is deemed suitable for irrigation purposes (Jeyaseelan *et al*., 2013).The %Na in this study ranged from 37.00 to 75.30% with an average of 50.64% (Appendix 4).The classification of groundwater from the study area based on %Na is presented in (Table .). Based of %Na, 4 samples representing 8% (Table .) had valuesbetween 20 and 40 and were classified good for irrigation. Thirty-three (41) samples representing 82% had %Na between 40 and 60 and were deemed permissible.Five samples which translated into 10% were classified as doubtful and had %Na between 60 and 80.

Table .: Classification of groundwater from the study based on %Na

% Na	Class of Water	No. of Samples	% of Samples
< 20	Excellent	Nil	Nil
20-40	Good	4	8
40-60	Permissible	41	82
60-80	Doubtful	5	10
> 80	Unsuitable	Nil	Nil

To further access the groundwater quality for irrigation, the calculated %Na was plotted as a function of EC(Wilcox plot, Figure .). The Wilcox plot (Figure .) classified all sample as excellent to good for irrigation.

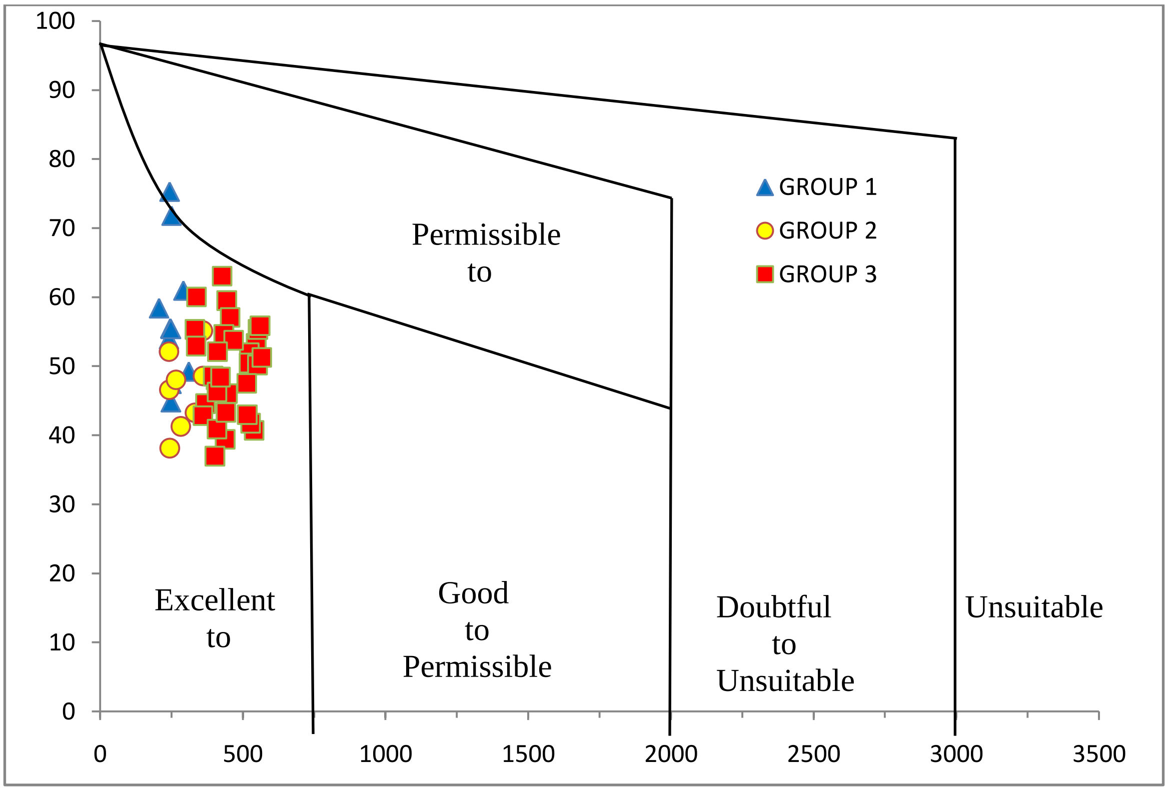


Figure .: Wilcox diagram for classifying groundwater samples based on %Na and EC

5.2.7.4 Magnesium Hazard

Magnesium is believed to be injurious to plants and can adversely affect crops yield when it is in equilibrium state in natural waters. However, this hazardous effect can be effectively minimized by the presence of Na and Ca(Nagaraju*et al*., 2006; Kortatsi *et al*., 2009). Magnesium hazard was proposed by Szabolc andDarab (1964) and defined as:

$$MgH = \frac{Mg\ (meq/L)}{Ca\ (meq/L) + Mg\ (meq/L)}\ x\ 100 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(.)}$$

MgH> 50% in irrigation water is considered to be harmful to most crops and hence deemed unsuitable for irrigation.The overall results obtained in this study, showed that 94% of the groundwater samples had MgH values < 50%and were suitable for irrigation whiles 6% had MgH>50% and suggested the potential MgHwhen used or irrigation.Details of the results of MgH has been presented in

Table .: Groundwater classification based on Magnesium hazard (MgH)

Percentage of Samples			MgH	Class of Water
Group 1	Group 2	Group 3		
90	87	98	<50%	Suitable
10	13	2	>50%	Unsuitable

5.2.7.5 Residual Sodium Carbonate (RSC)

Residual sodium carbonate is a measure of the difference between the excess sum of carbonate and bicarbonate in groundwater against the sum of calcium and magnesium. Just as SAR and %Na, it has significant effect on the suitability of groundwater for irrigation (Sundaray *et al*., 2009). High excess carbonate concentration often referred to as “residual” has the tendency to combine with calcium and magnesium to form a solid scale-like material which settles out of the water and this is known to deteriorate water quality (Sundaray *et al*., 2009). Residual sodium carbonate can be estimated by Equation 5.11(Richard, 1954):

$$\boldsymbol{RSC = \left(HCO_3^- + CO_3^{2-}\right) - (Ca^{2+} + Mg^{2+})} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{(.)}$$

where all units are expressed in meq/L.

RSC <1.25 meq/L is safe for irrigation, values between 1.25 to 2.5meq/L are of marginal quality and a value >2.5 meq/L is unsuitable for irrigation (Nagaraju*et al*., 2006). The RSC of groundwater in this study ranged from 0.54 to 3.04 with an average of 1.46 (Appendix 4).Thisimplied that the groundwater in the study ranged from safe to unsuitable for irrigation.The results of RSC has been summarised in Table ..

Table .:Suitability of water in the study area for irrigation based on RSC

Percentage of Samples			RSC	Class of Water
Group 1	Group 2	Group 3		
100%	63%	31%	<1.25%	Suitable
Nil	37	56	1.25-2.5%	Marginal
Nil	Nil	13	>2.5	Unsuitable

5.3 Summary of Findings

Groundwater recharge estimation in the study area by WBM and CMB method produced recharge rate of 6% and 5.7% of mean annual rainfall. These were found to be within the rangeof 2 to 13% of mean annual rainfall obtained by Martin (2006).

Physico-chemical parameters of groundwater (pH, TDS, EC, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^-, and HCO_3^-) and trace elements (Pb, Cd, As, Zn, F^-, Cu, Sb, Cr, Co, Fe, Ni and Mn) were successfully determined. Analysis of the hydrochemical data area revealed the groundwater was generally near neutral. The general trend of major cations and anions were $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$ and $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ respectively. Geochemical assessment of major ions using bi-plots suggested that, the occurrence of dissolved ions in groundwater in the study area were mainly controlled by dissolution of silicate minerals and ion exchange reactions.

Principal component analysis (PCA) of major ions showed that the groundwater quality in the Atankwidi Catchment was mainly controlled by rock water interactions and anthropogenic activities to some extent. Gibbs diagram for groundwater from the study area supported the PCA. The Hierarchical Cluster Analysis (HCA) further classified the groundwater of the study area into three groups. The most distinguishing factor among the groups seemed to be TDS which generally increased from group one to three.

Piper diagram of the groundwater samples also classified groundwater in the Atankwidi Catchmentarea into three mainhydrochemicalfacies namely Na-Ca-HCO_3, Na-Ca-Mg-HCO_3, and Na-HCO_3. The occurrence of these facies was mainly attributed to rock water interactions. This was supported by the PCA and Gibbs diagram.

The concentrations of trace elements analysed were generally within the WHO guidelines for drinking-water. Based on the water quality index, groundwater water from the study area was generally suitable for drinking.

The suitability of water from the study area for irrigation was assessed using the salinity index, United States Salinity Laboratory(USSL) diagram, percentage sodium, Wilcox diagram, magnesium hazard and residual sodium carbonate (RSC). The result showed that, groundwater samples were generally suitable for irrigation on wide range of soils. However, magnesium hazard and RSC problems are likely to limit its use.

CHAPTER SIX

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

The rate of groundwater recharge in the Atankwidi Catchment was successfully estimated using water balance and chloride mas balance methods. Recharge rate estimation by WBM and CMB methods were 6% and 5.7% respectively. The general trend of major cations and anions were $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$ and $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ respectively.Geochemical assessment of major ions using bi-plots revealed that, the presence of these ions in groundwater from the study area were largely controlled by rock water interactions and to a lesser extent anthropogenic activities and this was supported by principal component analysis of major ions and Gibbs plot.Hierarchical Cluster Analysis (HCA) grouped groundwater in the Atankwidi Catchment into three groups. The most distinguishing factor among the groups was TDS which generally increased from group one to three. Furthermore, based on Piper diagram, groundwater in this study was classified into three hydrochemicalfaices asNa-Ca-HCO_3, Na-Ca-Mg-HCO_3 and Na-HCO_3. The quality of groundwater in the study was determined to be good for drinking based on the trace elements concentrations and the overall water quality index. Also, the groundwater water quality was generally suitable for irrigation on wide range of soils based on the salinity index, USSL diagram, sodium percentage, and Wilcox diagram. However, problems associated with magnesium hazard and residual sodium carbonate is likely to limit groundwater use for irrigation.

6.2 Recommendations

The larger population in the AtankwidiBasin depend mostlyon groundwater to improve upon their socio-economic development therefore the following recommendations are made:

A comprehensive groundwater recharge study in the Atankwidi Catchment should be encouraged to help identity the recharge zones in the entire catchment, so that appropriate steps could be taken to protect such zones from pollution.

Also, farming is the major land use activity in the Atankwidi Catchment and agricultural activities through the application if agro-chemicals can pose serious threat to groundwater. Therefore, good agricultural practices should be encouraged in the catchment area in order to protect the groundwater from pollution.

Lastly, groundwater quality at AtankwidiCatchemnt was found to suitable for domestic and irrigation purposes hence rcommended for use as such.

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APPENDICES

Appendix 1: Charge Balance Error [all units in Keq/L, except CBE (%)]

Sample	Na	K	Ca	Mg	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	TZ^+	TZ^-	CBE
AK08	1.53	0.06	0.81	0.70	1.98	0.53	0.34	0.00	3.10	2.85	4.27
AK09	2.09	0.09	1.97	1.18	3.59	1.03	0.23	0.00	5.33	4.85	4.72
BAL01	2.00	0.26	1.39	0.84	3.63	0.22	0.23	0.00	4.49	4.07	4.89
BAL02	2.23	0.09	1.12	0.75	3.04	0.41	0.34	0.00	4.18	3.79	4.95
BAL03	2.00	0.01	0.96	0.63	2.86	0.48	0.34	0.00	3.60	3.68	-1.04
KAN01	2.33	0.18	1.47	0.98	3.32	0.73	0.90	0.00	4.96	4.95	0.02
KAN03	3.31	0.34	0.88	0.58	3.56	0.91	0.68	0.00	5.11	5.14	-0.35
KAN05	3.20	0.14	1.04	0.69	3.76	0.27	0.56	0.00	5.06	4.59	4.92
KAN07	2.27	0.30	0.65	0.43	2.71	0.15	0.67	0.00	3.65	3.54	1.55
KAN09	3.06	0.18	1.28	0.77	3.48	0.77	0.56	0.00	5.29	4.81	4.81
KAN12	2.48	0.12	1.82	1.21	4.35	0.83	0.67	0.00	5.64	5.85	-1.87
KAN14	3.09	0.16	1.92	1.23	4.03	1.00	0.78	0.00	6.40	5.81	4.81
KAN16	2.22	0.17	1.52	0.88	3.72	0.48	0.23	0.00	4.79	4.43	3.89
NAG02	3.34	0.19	1.50	1.00	4.43	0.97	0.23	0.00	6.03	5.62	3.48
NAG03	2.52	0.09	0.86	0.60	2.90	0.25	0.56	0.00	4.08	3.71	4.78
NAG05	2.81	0.14	1.63	1.08	3.89	0.91	0.35	0.00	5.66	5.15	4.71
NAG07	2.86	0.11	0.55	0.37	2.92	0.39	0.23	0.00	3.88	3.54	4.50
NAG08	2.30	0.10	1.47	0.98	3.80	0.37	0.23	0.00	4.85	4.39	4.96
NAG09	2.87	0.08	1.84	1.26	4.44	0.73	0.34	0.00	6.05	5.51	4.71
NAG10	2.97	0.14	1.54	0.93	4.18	0.42	0.45	0.00	5.57	5.06	4.83
SOM05	1.81	0.06	2.45	1.68	4.49	0.73	0.23	0.01	6.00	5.45	4.81
SOM01	1.45	0.19	1.06	0.70	2.80	0.12	0.46	0.00	3.40	3.38	0.25
SOM02	2.25	0.15	0.33	0.22	2.46	0.19	0.34	0.00	2.95	2.99	-0.76
SOM03	1.95	0.14	1.86	1.23	3.68	0.31	0.79	0.00	5.18	4.78	4.00
SOM04	2.49	0.07	1.25	0.84	4.08	0.35	0.23	0.00	4.65	4.65	-0.07
SRI01	2.63	0.13	1.03	0.68	3.81	0.06	0.23	0.00	4.47	4.10	4.28
SRI03	1.93	0.26	1.99	1.32	4.24	0.18	0.56	0.00	5.50	4.98	4.89
SRI05	1.88	0.11	1.30	0.70	2.72	0.64	0.28	0.00	3.98	3.64	4.42
SRI07	2.45	0.15	0.54	0.36	2.80	0.09	0.56	0.00	3.49	3.45	0.58
SRI09	1.68	0.18	0.88	0.59	2.56	0.09	0.67	0.00	3.33	3.32	0.26
SRI11	2.16	0.13	1.39	0.91	3.48	0.26	0.45	0.00	4.59	4.19	4.64
SRI13	1.61	0.06	2.05	1.37	3.78	0.50	0.34	0.00	5.09	4.61	4.97
SRI15	2.16	0.13	1.51	1.00	3.71	0.10	0.56	0.00	4.80	4.38	4.59
SRI17	2.78	0.10	1.43	0.98	4.28	0.32	0.23	0.00	5.29	4.83	4.55
SRI19	2.46	0.15	2.44	0.58	4.44	0.59	0.12	0.00	5.63	5.15	4.50
YUA01	2.07	0.17	2.15	1.47	4.27	0.93	0.23	0.00	5.85	5.43	3.75

Sample	**Na**	**K**	**Ca**	**Mg**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**	**NO_3^-**	**TZ^+**	**TZ^-**	**CBE**
YUA03	1.91	0.11	1.54	0.98	3.29	0.36	0.54	0.00	4.55	4.19	4.05
YUA06	2.85	0.16	2.15	1.33	4.43	1.04	0.44	0.00	6.49	5.90	4.74
YUA07	1.95	0.17	2.08	1.38	4.38	0.51	0.23	0.00	5.57	5.12	4.24
YUA08	2.20	0.03	1.55	1.03	3.85	0.54	0.12	0.00	4.81	4.51	3.15
YUA09	3.20	0.12	1.68	1.15	4.43	0.94	0.23	0.00	6.15	5.60	4.66
ZOK01	2.20	0.13	1.05	0.70	2.80	0.56	0.34	0.00	4.08	3.70	4.95
ZOK03	1.77	0.13	1.36	0.90	3.83	0.08	0.23	0.00	4.16	4.13	0.28
ZOK05	2.33	0.18	1.47	0.98	3.25	0.60	1.13	0.00	4.95	4.98	-0.34
ZOK07	2.86	0.11	1.53	1.01	4.25	0.50	0.23	0.00	5.51	4.99	4.94
ZOK09	2.94	0.04	1.05	0.70	4.23	0.07	0.45	0.00	4.73	4.74	-0.13
ZOK10	2.53	0.06	1.41	0.89	3.77	0.49	0.23	0.00	4.88	4.49	4.22
ZOK12	2.00	0.15	1.72	1.09	3.49	0.56	0.45	0.00	4.96	4.51	4.72
ZOK15	2.02	0.11	1.84	1.26	3.74	0.71	0.34	0.00	5.23	4.79	4.34
ZOK16	2.49	0.07	0.59	0.22	2.32	0.17	0.66	0.00	3.36	3.15	3.23
Mean	**2.37**	**0.13**	**1.42**	**0.91**	**3.60**	**0.49**	**0.42**	**0.00**	**4.83**	**4.51**	**3.28**
Max	**3.34**	**0.34**	**2.45**	**1.68**	**4.49**	**1.04**	**1.13**	**0.01**	**6.49**	**5.90**	**4.97**
Min	**1.45**	**0.01**	**0.33**	**0.22**	**1.98**	**0.06**	**0.12**	**0.00**	**2.95**	**2.85**	**-1.87**

TZ^+ = total cations

TZ^- = total anions

Appendix 2: Sample Calculation of surface runoff

Month	T(mean) °C	r (mm/month)	T+273.15	e_0=1.0 x 10^9exp(-4.62×10^3 /T + 273.15)	Qs(m^3)= 10^3Ar[exp(e_o/ r)]	Qs (mm) = Qs (m^3)/A (m^2)
JAN	27.85	0.16	301.00	215.867	0	0
FEB	30.42	2.29	303.57	245.797	1.4373E-41	5E-47
MAR	32.76	11.11	305.91	276.052	5.1669E-05	1.8E-10
APR	32.83	55.03	305.98	277.086	102348.389	0.35786
MAY	30.93	101.69	304.08	252.102	2437485.03	8.52267
JUN	28.62	136.69	301.77	224.416	7570367.34	26.4698
JUL	27.28	178.22	300.43	209.658	15717825.4	54.9574
AUG	26.74	269.14	299.89	203.875	36087201.7	126.179
SEP	27.13	165.08	300.28	208.021	13389669	46.817
OCT	28.60	50.38	301.75	224.174	168306.042	0.58848
NOV	28.86	3.23	302.01	227.191	2.6376E-25	9.2E-31
DEC	27.68	2.01	300.83	213.923	3.2869E-41	1.1E-46
Average	**29.14**	**81.25**	**302.29**	**231.514**	**6289433.58**	**21.991**
Max	**32.83**	**269.14**	**305.98**	**277.086**	**36087201.7**	**126.179**
Min	**26.74**	**0.16**	**299.89**	**203.875**	**0**	**0**

Qs(m^3)= 10^3Ar[exp($-e_o$/ r)]

e_0=10^9exp(-4.62×10^3 /T + 273.15)

A= catchment area, r= rainfall, T = temperature

Appendix 3A: Rainfall amounts and Cl$^-$ concentration in rainwater

S/N	ID	DATE	AMT OF RAINFALL(mm)	pH	EC (uS/cm)	TDS (mg/L)	Cl (mg/L)
1	RW16	27/06/2013	4.20	6.81	357.00	182.00	0.60
2	RW10	25/08/2013	17.70	6.05	19.54	9.70	1.40
3	RW12	30/08/2013	10.40	5.82	30.90	15.70	0.20
4	RW13	5/9/2013	19.80	6.40	30.30	15.30	0.20
5	RW15	14/09/2013	14.40	6.57	51.30	26.00	0.60
6	RW14	30/09/2013	10.30	6.50	221.00	110.80	1.39
7	RW17	3/10/2013	31.50	6.45	17.52	8.90	0.20
8	RW9	8/10/2013	31.00	6.20	22.40	11.20	0.61
9	RW11	22/10/2013	13.20	6.33	82.20	41.70	0.22
10	RW7	9/5/2014	1.80	6.54	185.50	93.60	1.00
11	RW8	4/6/2014	9.20	6.15	94.20	93.60	0.60
12	RW5	14/07/2014	10.60	5.77	27.00	13.50	1.39
12	RW6	18/07/2014	10.50	6.55	57.80	29.10	0.20
14	RW4	23/07/2014	21.60	6.27	139.40	71.00	0.60
15	RW3	15/08/2014	5.60	6.78	158.50	80.00	0.60
16	RW2	17/08/2014	5.60	5.53	227.00	115.00	0.20
17	RW1	19/08/2014	17.00	6.28	142.80	72.00	1.00
	Mean		**13.79**	**6.29**	**109.67**	**58.18**	**0.65**
	MAX		**31.50**	**6.81**	**357.00**	**182.00**	**1.40**
	MIN		**1.80**	**5.53**	**17.52**	**8.90**	**0.20**

Appendix 3B: Groundwater recharge by CMB (Clp = 0.65, mean annual rainfall = 996. 74 mm

Sample	LONG.	LAT.	Clgw (mg/L)	Clp/Clgw	% Clp/Clgw	Recharge mm/yr	% Recharge/yr
AK08	1199065	718974	12.12	0.05	5.36	53.47	5.4
AK09	1198902	719353	8.32	0.08	7.81	77.89	7.8
BAL01	1210437	731541	7.99	0.08	8.14	81.11	8.1
BAL02	1212146	731917	12.01	0.05	5.41	53.96	5.4
BAL03	1212647	733334	12.00	0.05	5.42	54.00	5.4
KAN01	1204581	722107	31.97	0.02	2.03	20.27	2.0
KAN03	1205636	722078	23.98	0.03	2.71	27.02	2.7
KAN05	1206266	721445	19.96	0.03	3.26	32.47	3.3
KAN07	1208475	723211	23.95	0.03	2.71	27.06	2.7
KAN09	1213731	728040	19.99	0.03	3.25	32.42	3.3
KAN12	1204615	724032	23.89	0.03	2.72	27.13	2.7
KAN14	1205547	723040	27.69	0.02	2.35	23.40	2.3
KAN16	1203434	725288	8.10	0.08	8.02	80.01	8.0
NAG02	1211354	722871	8.10	0.08	8.02	80.01	8.0
NAG03	1212813	723037	19.79	0.03	3.28	32.75	3.3
NAG05	1210437	723079	12.44	0.05	5.23	52.09	5.2
NAG07	1209437	725372	8.12	0.08	8.00	79.81	8.0
NAG08	1213647	723162	8.10	0.08	8.02	80.01	8.0
NAG09	1213138	724079	12.00	0.05	5.42	54.00	5.4
NAG10	1214474	723234	15.99	0.04	4.07	40.53	4.1
S0M05	1201141	723371	8.00	0.08	8.13	81.01	8.1
SOM01	1203392	727623	16.24	0.04	4.00	39.90	4.0
SOM02	1202850	722829	12.00	0.05	5.42	54.00	5.4
SOM03	1201558	721120	27.95	0.02	2.33	23.19	2.3
SOM04	1199807	722162	8.00	0.08	8.13	81.01	8.1
SRI01	1212110	723925	8.00	0.08	8.13	81.01	8.1
SRI03	1210972	724268	19.99	0.03	3.25	32.42	3.3
SRI05	1210630	725262	10.00	0.07	6.50	64.81	6.5
SRI07	1211304	726046	19.99	0.03	3.25	32.42	3.3
SRI09	1209898	726334	23.95	0.03	2.71	27.06	2.7
SRI11	1211878	726991	15.91	0.04	4.09	40.73	4.1
SRI13	1212057	727693	12.00	0.05	5.42	54.00	5.4
SRI15	1213537	727584	19.97	0.03	3.25	32.45	3.3
SRI17	1212310	725626	8.00	0.08	8.13	81.01	8.1
SRI19	1214488	725473	4.10	0.16	15.85	158.06	15.9
YUA01	1213689	728498	8.00	0.08	8.13	81.01	8.1
YUA03	1214684	726622	19.29	0.03	3.37	33.60	3.4
YUA06	1212980	727915	15.49	0.04	4.20	41.84	4.2
Sample	**LONG.**	**LAT.**	**Clgw**	**Clp/Clgw**	**%**	**Recharge**	**%**

			(mg/L)		Clp/Clgw	mm/yr	Recharge/yr
YUA07	1212497	729187	8.00	0.08	8.13	81.01	8.1
YUA08	1212406	728317	4.10	0.16	15.85	158.06	15.9
YUA09	1211605	729582	8.00	0.08	8.13	81.01	8.1
ZOK01	1209214	727700	12.11	0.05	5.37	53.51	5.4
ZOK03	1207519	726539	8.10	0.08	8.02	80.01	8.0
ZOK05	1206441	729179	39.97	0.02	1.63	16.21	1.6
ZOK07	1205893	726414	8.31	0.08	7.82	77.98	7.8
ZOK09	1205085	728138	15.91	0.04	4.09	40.73	4.1
ZOK10	1205351	727679	8.20	0.08	7.93	79.03	7.9
ZOK12	1207173	729286	16.11	0.04	4.03	40.23	4.0
ZOK15	1206793	731033	12.13	0.05	5.36	53.43	5.4
ZOK16	1205435	730333	23.59	0.03	2.76	27.47	2.8
Mean	1208710	725838	14.76	0.06	5.69	56.75	5.7
Max	1214684	733334	39.97	0.16	15.85	158.06	15.9
Min	1198902	718974	4.10	0.02	1.63	16.21	1.6

Appendix 4: Na/Cl, CA1, CA2, Na/Na+Cl, Cl/TZ$^-$, SAR, %Na, MgH and RSC

Sample	Na/Cl	CA1	CA2	Na/ Na+Cl	Cl/TZ$^-$	SAR	Na%	MgH	RSC
AK008	4.50	-3.68	-0.50	0.82	0.12	1.77	51.44	46.24	0.47
AK009	8.92	-8.30	-0.42	0.90	0.05	1.67	40.87	37.44	0.44
BAL001	8.89	-9.04	-0.53	0.90	0.06	1.89	50.29	37.76	1.39
BAL002	6.58	-5.85	-0.57	0.87	0.09	2.31	55.43	39.96	1.17
BAL003	5.92	-4.93	-0.50	0.86	0.09	2.24	55.71	39.72	1.26
KAN001	2.58	-1.78	-0.40	0.72	0.18	2.10	50.55	39.98	0.87
KAN003	4.90	-4.40	-0.66	0.83	0.13	3.87	71.41	39.95	2.10
KAN005	5.68	-4.93	-0.69	0.85	0.12	3.44	65.92	40.00	2.03
KAN007	3.37	-2.81	-0.66	0.77	0.19	3.10	70.50	39.96	1.64
KAN009	5.44	-4.76	-0.63	0.84	0.12	3.02	61.26	37.54	1.43
KAN012	3.69	-2.87	-0.37	0.79	0.11	2.02	46.17	39.97	1.31
KAN014	3.96	-3.16	-0.49	0.80	0.13	2.46	50.75	39.03	0.88
KAN016	9.74	-9.47	-0.51	0.91	0.05	2.03	49.87	36.66	1.32
NAG002	14.63	-14.47	-0.61	0.94	0.04	2.99	58.53	40.00	1.93
NAG003	4.52	-3.69	-0.65	0.82	0.15	2.95	64.18	41.31	1.44
NAG005	8.03	-7.42	-0.54	0.89	0.07	2.42	52.13	39.96	1.18
NAG007	12.49	-11.95	-0.82	0.93	0.06	4.22	76.35	39.98	2.01
NAG008	10.06	-9.50	-0.52	0.91	0.05	2.07	49.40	39.94	1.34
NAG009	8.49	-7.74	-0.51	0.89	0.06	2.31	48.83	40.65	1.34
NAG010	6.58	-5.88	-0.58	0.87	0.09	2.67	55.68	37.54	1.71
SOM005	8.03	-7.29	-0.31	0.89	0.04	1.26	31.11	40.70	0.36
SOM001	3.17	-2.59	-0.41	0.76	0.14	1.55	48.34	39.89	1.04
SOM002	6.65	-6.08	-0.77	0.87	0.11	4.28	81.25	39.82	1.91
SOM003	2.47	-1.65	-0.33	0.71	0.16	1.57	40.31	39.92	0.59
SOM004	11.04	-10.35	-0.53	0.92	0.05	2.43	55.07	40.00	1.99
SRI001	11.67	-11.23	-0.65	0.92	0.05	2.85	61.72	39.98	2.10
SRI003	3.43	-2.88	-0.37	0.77	0.11	1.50	39.79	39.99	0.93
SRI005	6.67	-6.06	-0.51	0.87	0.08	1.88	49.94	34.95	0.73
SRI007	4.35	-3.62	-0.70	0.81	0.16	3.66	74.42	39.93	1.90
SRI009	2.49	-1.76	-0.45	0.71	0.20	1.95	55.78	40.01	1.08
SRI011	4.82	-4.10	-0.49	0.83	0.11	2.01	49.78	39.60	1.17
SRI013	4.76	-3.94	-0.31	0.83	0.07	1.23	32.79	40.02	0.35
SRI015	3.84	-3.07	-0.45	0.79	0.13	1.93	47.74	39.99	1.20
SRI017	12.33	-11.78	-0.58	0.92	0.05	2.53	54.44	40.79	1.87
SRI019	21.31	-21.64	-0.50	0.96	0.02	2.00	46.41	19.10	1.42
YUA001	9.16	-8.90	-0.39	0.90	0.04	1.54	38.15	40.52	0.65
YUA003	3.52	-2.72	-0.41	0.78	0.13	1.70	44.49	38.82	0.77
YUA006	6.53	-5.89	-0.47	0.87	0.07	2.16	46.34	38.30	0.95
YUA007	8.64	-8.38	-0.39	0.90	0.04	1.48	37.94	39.99	0.92
YUA008	19.01	-18.23	-0.48	0.95	0.03	1.93	46.21	39.97	1.27

Sample	Na/Cl	CA1	CA2	Na/ Na+Cl	Cl/TZ^-	SAR	Na%	MgH	RSC
YUA009	14.20	-13.75	-0.58	0.93	0.04	2.69	54.05	40.71	1.61
ZOK001	6.45	-5.83	-0.59	0.87	0.09	2.35	57.03	39.90	1.04
ZOK003	7.76	-7.32	-0.43	0.89	0.06	1.66	45.65	39.98	1.57
ZOK005	2.07	-1.23	-0.36	0.67	0.23	2.10	50.62	39.96	0.81
ZOK007	12.20	-11.68	-0.57	0.92	0.05	2.53	53.90	39.90	1.71
ZOK009	6.57	-5.65	-0.59	0.87	0.09	3.14	62.96	39.94	2.47
ZOK010	10.95	-10.22	-0.55	0.92	0.05	2.36	53.07	38.69	1.48
ZOK012	4.41	-3.73	-0.42	0.82	0.10	1.69	43.30	38.91	0.68
ZOK015	5.92	-5.23	-0.40	0.86	0.07	1.62	40.72	40.65	0.64
ZOK016	3.74	-2.84	-0.76	0.79	0.21	3.91	75.96	27.23	1.51
Mean	**7.34**	**-6.73**	**-0.52**	**0.85**	**0.10**	**2.34**	**52.89**	**39.04**	**1.28**
Max	**21.31**	**-1.23**	**-0.31**	**0.96**	**0.23**	**4.28**	**81.25**	**46.24**	**2.47**
Min	**2.07**	**-21.64**	**-0.82**	**0.67**	**0.02**	**1.23**	**31.11**	**19.10**	**0.35**

Appendix 5A: Groundwater quality Index (GWQI)

Sample	GQWQI	REMARKS
AK08	2.14	Excellent
AK09	8.24	Excellent
BAL01	21.05	Excellent
BAL02	67.06	Poor
BAL03	28.77	Good
KAN01	0.28	Excellent
KAN03	26.59	Good
KAN05	27.18	Good
KAN07	44.96	Good
KAN09	43.70	Good
KAN12	4.13	Excellent
KAN14	8.08	Excellent
KAN16	15.49	Excellent
NAG02	29.19	Good
NAG03	4.57	Excellent
NAG05	30.84	Good
NAG07	27.80	Good
NAG08	0.29	Excellent
NAG09	24.23	Excellent
NAG10	0.22	Excellent
SOM05	76.02	Bad
SOM01	0.14	Excellent
SOM02	13.32	Excellent
SOM03	0.02	Excellent
SOM04	60.85	Poor
SRI01	4.03	Excellent
SRI03	3.94	Excellent
SRI05	15.04	Excellent
SRI07	27.08	Good
SRI09	6.16	Excellent
SRI11	46.55	Good
SRI13	50.82	Poor
SRI15	30.90	Good
SRI17	34.10	Good
SRI19	0.06	Excellent
YUA01	8.41	Excellent
YUA03	32.16	Good
YUA06	37.71	Good
YUA07	0.23	Excellent
YUA08	4.08	Excellent
YUA09	4.55	Excellent

Sample	GQWQI	REMARKS
ZOK01	9.69	Excellent
ZOK03	0.25	Excellent
ZOK05	25.50	Good
ZOK07	4.68	Excellent
ZOK09	8.57	Excellent
ZOK10	22.06	Excellent
ZOK12	0.06	Excellent
ZOK15	10.40	Excellent
ZOK16	44.52	Good
Mean	**19.93**	
Max	**76.02**	
Min	**0.06**	

Appendix 5B: Sample calculation for WQI

Parameters	Mean values (mg/L)	Standard permissible limit Value (S_i)	Ideal Value (V_i)	Unit weight (W_i= 1/S_i)	Quality rating (Q_i)	Q_i*Wi
	6.94	8.5	7	0.118	-4.000	-0.47
	394.62	500	0	0.002	78.924	0.16
	276	1000	0	0.001	27.600	0.03
	219.77	500	0	0.002	43.954	0.09
	28.41	100	0	0.010	28.410	0.28
	10.89	30	0	0.033	36.300	1.21
	54.5	200	0	0.005	27.250	0.14
	5.2	10	0	0.100	52.000	5.20
	0.75	1.5	1	0.667	50.000	33.33
	14.76	250	0	0.004	5.904	0.02
	23.51	400	0	0.003	5.878	0.01
	0.06	45	0	0.022	0.133	0.00
	0	0.01	0	100.000	0.000	0.00
	0	0.01	0	100.000	0.000	0.00
	0.1	2	0	0.500	5.000	2.50
	0.02	0.02	0	50.000	100.000	5000.00
	0	0.01	0	100.000	0.000	0.00
				351.466		**5042.51**

W $= \frac{5042.51}{351.47}$ = 14. 35