ESTIMATION OF GROUNDWATER RECHARGE IN GUSHIEGU AND SURROUNDING AREAS

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FACULTY OF SCIENCE
UNIVERSITY OF GHANA

MPhil

JULY 2013

Estimation of Groundwater Recharge in the Gushiegu and Surrounding areas

This Thesis is Submitted to the:

DEPARTMENT OF EARTH SCIENCE

FACULTY OF SCIENCE

UNIVERSITY OF GHANA, LEGON

By

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In partial fulfillment of the requirements for the award of

MASTER OF PHILOSOPHY

In

GEOLOGY DEGREE.

July, 2013

DECLARATION

This thesis is the result of research work undertaken by Afrifa, George Yamoah, under supervision towards the award of Master of Philosophy in Geology. The research was done based on the requirement of the Graduate School, University of Ghana, Legon.

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ABSTRACT

Gushiegu and surrounding areas are lowland terrain underlain by the Voltaian System which consists of medium grains sandstones, micaceous sandstones, interbedded mudstones, siltstones and shales. Lack of perennial surface water has led to most of the communities in the area relying solely on groundwater as source of water for domestic and commercial use. Over abstraction of groundwater can cause significant drawdown of the hydraulic heads leading to significant ecological consequences. In other to avoid these consequences, proper management of groundwater resource in the area is encouraged. This begins with fairly accurate estimation of groundwater recharge; identification of recharge areas and the source of groundwater recharge.

This study was therefore carried out to estimate the groundwater recharge and its spatial variations in the study area using Chloride Mass Balance (CMB) and Water Table Fluctuation (WTF) techniques. The CMB method suggests recharge in a range 13.9 mm/y to 218 mm/y with an average of 89 mm/yr which translates into about 1.3% to 21.8 % of the annual precipitation in the area, with an average of 8.9%. The low recharge rate may be attributed to the geological characteristic of the unsaturated zone material. Inverse Distance Weighting (IDW) was applied to predict the spatial variation of the estimated groundwater recharge. The same interpolation technique was applied to isotopic composition of the groundwater to predict the spatial variation using Surfer 9. The predicted map of the estimated groundwater recharge suggests that the southwestern and northeastern part of the study area is most recharged. The highest recharge rates are associated with areas where open wells encourage significant amount of groundwater recharge from precipitation in the area. The WTF technique applied to two monitoring wells also suggest a cumulative average groundwater recharge of 71.4 mm/yr and 81.0 mm/yr which translate into 7.14 % and 8.1 % of the annual precipitation. These figures agree with the values obtained by the CMB technique.

Isotopic data of precipitation and groundwater were used to infer the origin and the possible relationship between groundwater and surface water in the partially metamorphosed sedimentary aquifer system in the Gushiegu area. Though, the data does not significantly establish potent relation between groundwater and surface water. The study suggests that groundwater in the area is of meteoric origin. However, the data suggests significant enrichment of the heavier isotopes in groundwater relative to rainwater in the region. The high level of evaporative enrichment of the groundwater was observed because the unsaturated zone in the study area has been noted for significant clay fractions which retard the vertical infiltration and percolation of precipitation. This leading to significant proportion of the annual rainfall lost through evapotranspiration and runoff. The low EC (68.4 – 1114 µS/cm) values lend credence to the suggestion that the groundwater is of meteoric origin.

DEDICATION

I dedicate this work to my mum, Madam Mercy Owusu for her financial support, encouragement and above all her love. Her spiritual support cannot also be precluded.

ACKNOWLEDGEMENT

My deepest gratitude goes to the Almighty God for His mercy and guidance. Thank you God for fulfilling your part of the covenant, though I could not keep mine to the latter. Your mercy endures forever.

Secondly, I would like to express my heartfelt gratitude to my supervisors Dr. Mark Sandow Yidana and Dr. Patrick Asamoah Sakyi for their immense supervision and constructive criticisms in making this thesis work a success. Not for getting the "can do spirit" they impacted in me, when I thought all hope was lost. The impact you have made in my life makes me feel so refined and confident to face the future. Thank you so much.

I would also like to say thank you to Prof. P.M. Nude and Dr. Thomas Armah at the Earth Science Department for their encouragement and Mr. Asare at the Water Resource Commission for the water level data.

I am grateful to my colleagues Michael Fiifi Dumolga, Alfred Prempeh Amoako and Belinda Seyram Berdie. A very big thank you also goes to all MPhil students who have played various roles in my academic pursuit, especially Daniel Kwayisi, Gloria Awo Senyah, Abigail Ayikwei and Millicent Obeng Addai.

I would also like to thank my parents - Mr. Kwabena Afrifa Yamoah and Mother Mercy Owusu, and all my siblings for their love, support, encouragement and prayers.

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CHAPTER ONE

INRODUCTION

1.1 Background

Groundwater is a significant part of the total water resources in the world. It plays one of the major roles in economic development. The use of groundwater as an alternate source of portable water supply is increasing, and in Ghana 62 – 71 % of the rural and suburban water comes from this resource (GEM/Water Project, 1997).

Groundwater is preferred to surface water in relation to development because it has vast reserves and broad geographical distribution, good quality and requires minimal or no treatment prior to usage. The resource is also protected from contamination from surface activities and above all it costs far less to develop. Groundwater can be tapped at relatively shallow depths at comparatively modest costs and, thus, serves as a reliable resource within the economic reach of rural communities (Attandoh et al., 2012). The capital cost of exploiting groundwater is modest compared to treating contaminated surface waters before use (Yidana, 2010).

Groundwater recharge characterization is more critical in sustainable management of water and helps in the control of subsurface contamination. It is well known that the primary controls on recharge are meteorology, soil properties, vegetation, and topography. These controls interact to create the distinctive conditions that result in recharge (Ng et al., 2009). Uncertainties about these control mechanisms make it difficult to predict long-term effects of climate change, meteorological variability, and land use change on groundwater resources (Ng et al., 2009).

The Gushiegu District, which is located in the northeastern corridor of the Northern Region of Ghana, relies mostly on groundwater to meet the increasing demand for domestic, irrigational and industrial use, because it is the most widely available source of fresh water in the area. This is due to lack of permanent surface water reservoirs owing to the harsh prevailing climatic conditions (GDWSP, 2008; SEA, 2010). There is no major river in the district except tributaries and sub-tributaries of Nasia, Daka, Nabogu and Oti Rivers which run through the district, but they are also seasonal (Abdul-Ganiyu et al., 2011). Due to the dependency on groundwater for all these purposes, a good estimation of groundwater recharge using Chloride Mass-balance (CMB), Water Table Fluctuation (WTF) and isotopic analysis will help to effectively manage the aquifer system.

Management with a goal of sustainable yield requires a better understanding of the sophisticated processes that determine the quantity and quality of groundwater systems, their interaction with the surface environment and subsurface geology, and the potential impacts of using these systems for water supply.

1.2 Statement of the Problem

In Ghana most rural settlements have traditionally rely on raw surface water from sources such as streams, rivers, lakes, ponds, dug-outs and impoundment reservoirs, and most of these sources are usually highly polluted, resulting in water-borne and water- related diseases such as diarrhea, guinea worm, bilharzias, etc. (Gyau-Boakye and Dapaah-Siakwan, 2000). Most part of the northern Ghana is characterized by prolong dry season and so most areas do not have access to surface water. The communities in the Gushiegu District located in these areas do not have much access to surface water because most streams in the area including major tributaries either dry up or have very little flow in the prolonged dry season. As a result about 54% of the people in the community are without access to portable water (GDWSP, 2008).

Based on these, the Government of Ghana has undertaken projects aimed at exploring groundwater for rural communities by the year 2020 (Ghana-Vision, 2020). The government's aim at supplying groundwater to all rural communities may not be achieved if proper management measures are not taken to effectively regulate the abstraction of groundwater resources in rural communities like Gushiegu, whose population is increasing yearly. According to IWRMP (2008), the population of the Gushiegu District is estimated to be 236200 by 2025 based on an annual population growth rate of 3% per annum.

Rapid economic growth and lack of regular precipitation, may lead to dramatic increase in the use of groundwater resources, and over abstraction of groundwater has four serious consequences namely (Gyau-Boakye and Dapaah-Siakwan, 2000; Subyani, 2004):

(i) significant water-level decline;

(ii) increasing groundwater salinity;

(iii) desertification of grazing and agricultural lands; and

(iv) human migration to major cities.

Both domestic and agricultural activities can be sustained based on good management of groundwater storage without significant problems, especially in the semi-arid regions, like the Northern Region of Ghana where Gushiegu is located. Groundwater decline has been observed in the semi-arid northern part of Ghana and some areas in the south, leading to gradual depletion of the resource due to excessive reliance on groundwater resources (Gyau-Boakye and Dapaah-Siakwan, 2000). Groundwater can be mined in the same manner as minerals, whenever groundwater is withdrawn at a rate greater than the rate of replenishment (Fetter, 1994). However, little is known about the safe yield of the study area, which is the amount of naturally occurring groundwater that can be withdrawn from an aquifer on a sustained basis, economically and legally, without impairing the native groundwater quality or creating an undesirable effect such as environmental damage (Fetter, 1994).

Therefore quality of groundwater, the source of recharge, flow path and quantity of groundwater which can be abstracted for socio-economic development must be known and documented for further studies.

1.3 Objectives

The main objectives of the research are to:

- Quantify the groundwater recharge and its spatial variability using Chloride Mass Balance and Water Table Fluctuation methods.
- Constrain the recharge estimated using natural tracers (δ^2H and $\delta^{18}O$).
- Develop a local groundwater line (LGWL) for the Voltaian aquifer.
- Develop a recharge map and water-table hydrograph; this will help estimate recharge and to establish a relation between rainfall events and recharge.

1.4 Justification

Groundwater recharge is critical for assessing the quantity and quality of water available. Accurate estimation of groundwater recharge is an important aspect of managing groundwater systems, in order to prevent significant declines in the water table since most parts of Gushiegu depend on groundwater abstraction for domestic and commercial activities. Estimation of ground water recharge within the district would also help identify recharge and discharge areas and good measures to be taken to protect such zones from contamination.

The rate and location of groundwater recharge are primary factors in determining sustainable yield of an aquifer. In arid and semiarid regions, recharge fluxes are often a very small percentage of the total precipitation falling over the basin and are highly heterogeneous in space and time (Wilson and Guan, 2004). Quantifying these fluxes and understanding the geological controls on recharge processes are critical components in the development of a comprehensive conceptual model of an aquifer system (Druhan et al., 2007). This conceptual model in turn serves as the foundation for analyses to determine appropriate pumping locations and rates, and, therefore, has a direct effect on the success of implementing sustainable management practices (Alley and Leake, 2004; Sophocleous, 2000). Communities which do not have “identified” recharged areas and land-use control would find it difficult protecting the aquifer from overdevelopment and contamination, mostly when transmitting water from far distance (Hordon, 1977).

The backbone of Ghana’s economy is agriculture, but due to prolonged dry season in northern Ghana and for that matter Gushiegu and surrounding areas, production from the agricultural sector is in a decline (GDACB, 2012). In view of this, the President’s Special Initiative (PSI) on agri-business - an initiative to support and strengthen the linkage between agriculture and industry has been launched (SEA, 2010). This initiative by the President of Ghana, aimed at producing sufficient raw materials for the available industries other than importing raw materials to feed these industry. It also aimed at self sufficiency in agricultural produce; thus, what the nation produces should be enough to feed her members and surplus left for export. For successful achievement of this program a good estimate of groundwater recharge will inform stakeholders and policy makers as to what to do to increase production.

1.5 Study Area

1.5.1 Location and Accessibility

The Gushiegu District is located in the north-eastern part of the Northern Region of Ghana, between latitude 9° 40'0″ and 10° 20'0″ North and longitudes 0°40′0″ W and 0°10′0″ E. The total land area of the district is approximately 5,796 km^2, and Gushiegu, the capital of the district is located at about 114 km from Tamale, the capital of the Northern Region of Ghana (Anim-Gyampo et al., 2012). The district has a population density of 22 persons per km^2 (Anim-Gyampo et al. 2012). It is bordered by six other districts in the region, namely; West Mamprusi and Karaga districts to the west, Saboba/Chereponi to the east, East Mamprusi and Bunkpurugu Yunyoo to the north, and Yendi to the South. According to the provisional results of the population and housing census released by the Ghana Statistical Service (2010), Gushiegu as a district has 111,256 inhabitants distributed within the 395 communities (Figure 1.1).

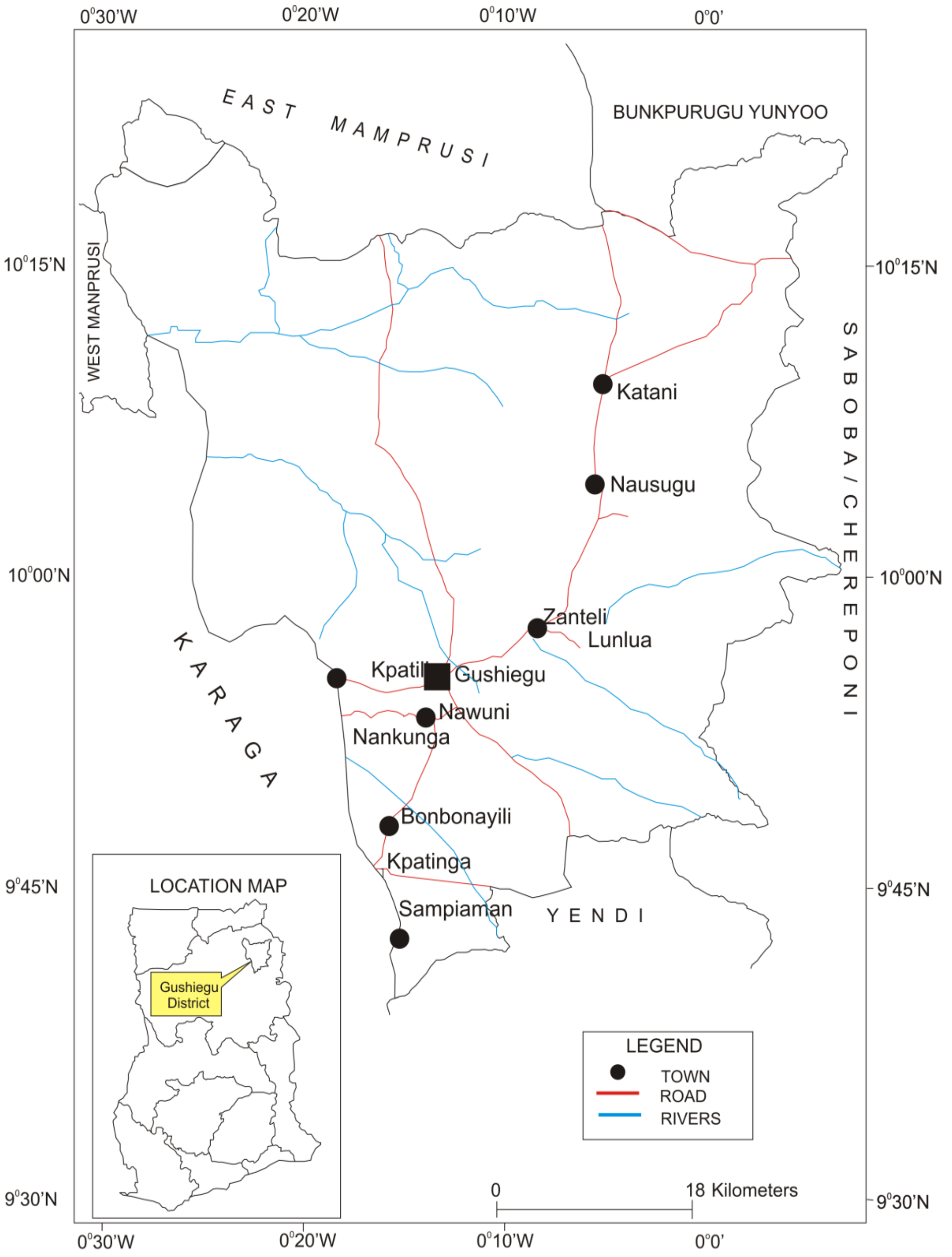


Figure 1.1. Location and geological map of Gushiegu District showing the various communities.

1.5.2 Climate, Vegetation and Drainage

Gushiegu District is located in the Northern Region of Ghana and is covered by a tropical climate marked by the alternation of dry and rainy season. However, when analyzing rainfall in Ghana, it is noticed that, as you move from south to north there is a gradual decrease in rainy season duration. An extremely dry dusty wind blows from the Sahara towards the western coast of Africa especially between November and March. These winds are predominantly characterized by the north-east trade winds in the form of harmattan which is hot and dry (SEA, 2010). The district has a unique rainy season pattern, which is influenced by south-east winds which lasts from May to October. Rainfalls vary between 900 mm and 1,000 mm and very heavy rainfall is recorded in July and August. Temperatures in the area are generally very high sometimes throughout the year. High temperature of about 40^{o} C are recorded between March and April and lowest temperatures between November and February (GDWSP, 2008; Anim-Gyampo et al., 2012).Gushiegu District is located in the Guinea savannah area which is characterized by short trees and grasses interspersed with drought resistant trees like shea nut, acacia, baobab, dawadawa, mango and neem (Anim-Gyampo et al., 2012).

There are no major rivers in the district, but tributaries and sub-tributaries of Nasia, Daka, Nabogu and Oti rivers run through the district. The main river that flows through the district between Nambrugu and Bagli is the Nasia, and the other streams found can be described as intermittent. The Nasia only reduces in volume during the long dry season, whereas all the other streams dry up completely. In the rainy season however, all the streams increase in volume and flood the immediate surrounding lands thereby cutting off most communities during the period. Most roads are also rendered unmotorable.

1.5.3 Soil

The principal soil type in the study area is of the forest ochrosols, which consist of coarse lateritic mountain soils and soft clay soils at the bottom of most valleys. Generally the forest ochrosols are slightly acidic in the topsoil (pH 5.1 – 6.5). Moderately to strongly acidic reactions have been encountered in the cultivated sites in this zone in recent times (Agyili et al., 1993; Dwomo and Asiamah, 1993; Asiamah et al., 2000; Pelig-Ba, 2000).

The study area is characterized by gentle slopes, making the soils highly vulnerable to sheet erosion, and in some areas, gully erosion also occurs. This condition occurs primarily because of annual burning of the natural vegetation, leaving the soil exposed to the normally high intense rainfall (up to 200 mm per hour) at the beginning of the rainy season (SEA, 2010). The continuous erosion over many years has removed most or all of the topsoil and depleted or destroyed its organic matter content (SEA, 2010). Such situation does not allow the soil fauna to thrive and keep the topsoil layers open and aerated for healthy plant roots to develop.

Unlike soils in the south, those northern savannahs where the Nasia basin is situated contain much less organic matter and are lower in nutrient than the forest soils (Adu, 1995). The laterites formed over granite, Voltaian shale and ochrosols form the main part of the savannah soils (Adu, 1995; Pelig-Ba, 2000).

1.5.4 Relief

The topography of the land is generally undulating with elevations ranging from 140m at valley bottoms to 180 m at highest plateaus. Being mostly watershed of main rivers, the district is endowed with many small valleys. Larger valleys can only be found towards the periphery of the district where the small streams merge into large ones. These large valleys can be found at Gaa, Katani, Sampemo and Sampegbiga areas. The size of all valleys in the district is estimated at 22,000 acres (Kesse, 1985, SEA 2010).

1.5.5 Geology

About one third of Ghana is covered by sediments of the inland Voltaian Basin which covers an area of about 103,600 km^2 (Kesse, 1985). Sedimentation of the Voltaian Group commenced about 1000 Ma ago; unconformably overlying a cratonic basement composed of rocks of the Birimain Supergroup and Tarkwaian Group rocks (Anani, 1999). Junner and Hirst (1946) subdivided the Voltaian sediments on the basis of lithology and field relationships into Lower, Middle and Upper units. The Voltaian is generally divided into three formations, each separated by an unconformity marked by a tillite. The Lower Voltaian Formation consists of a massive to cross-bedded arkosic sequence. The Middle Voltaian Formation consist of flyscoid sequence, and the Upper Voltaian Formation consist of a molasse sequence (Anani, 1999).

Most parts of the Gushiegu District is underlain by the Middle Voltaian sediments especially the northeastern part which recorded a glacial event followed by prolonged marine incursion and subsidence of the basin (; Trompette, 1981; Culver and Hunt, 1991; Porter et al., 2003). The northern tip of the District is underlain by the Bombouaka Mega-sequence which consists of fine to coarse-grained and more or less feldspathic sandstones (Fig. 1.2) (Bertrand-Sarfati et al., 1990). The Middle Voltaian Formation overlies the Lower Voltaian Formation with a slight angular unconformity and conglomeratic beds interpreted as tillites form the basal part of the Middle Voltaian Formation (Petters, 1991).

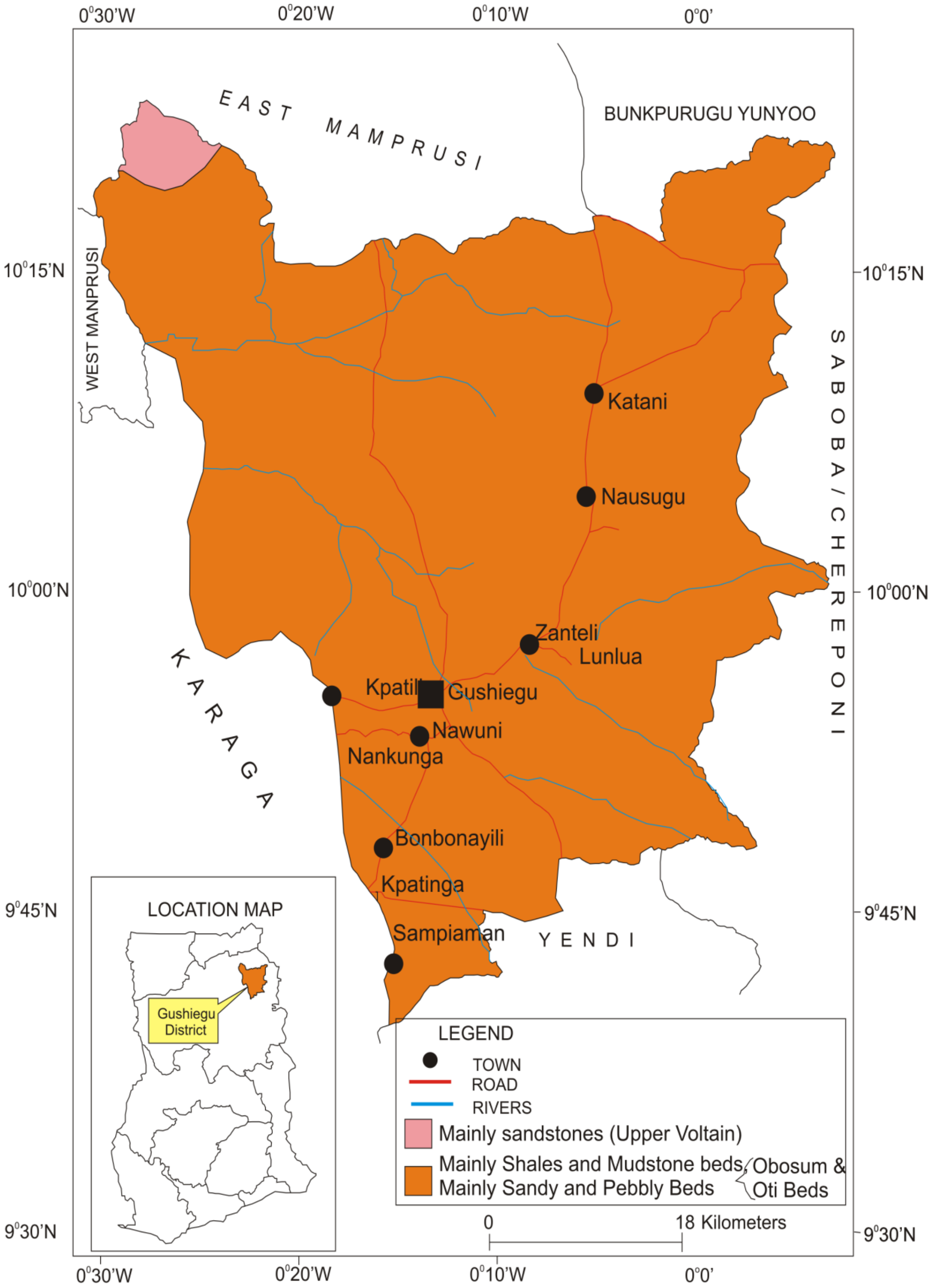


Fig.1. 2: Geological map of Gushiegu District

The Middle Voltaian basin is a sub-division of the paleozoic Voltaian sedimentary formation, specifically within the Kodjari formation of the Oti group which is highly heterogeneous in terms of lithology and dominated by quartzites, shales, mudstones, siltstones, conglomerates and limestones. This group overlies the Panabako formation of the Bombouaka Mega-sequence or the Lower Voltaian sub-division (Affaton et al., 1980; Wright et al., 1985; Hoffman, 1999). The conglomerates contain pebbles of granite and other igneous rocks, as well as quartzite fragments. Sedimentary structures show the direction of transport to have been from the southeast. According to Adu (1995), the Nasia catchment area is underlain by the Middle Voltaian system which consists of quartzite, shale, sandstone, limestone, conglomerate and arkose (Fig. 1.2). The average dip of the Voltaian rocks is 5^o, and the systems are gently folded.

Land Use

Various types of activities are conducted in Gushiegu District, but the most dominant one is agriculture. According to household surveys results, about 97% of the manpower are busy doing agriculture (SEA, 2010). The land tenure arrangement has positive enabling environment for agricultural investment in the district. The facts that land acquisition are not cumbersome and the fact that it is more or less freehold makes investment on agricultural sector in the district attractive. Besides crop production, the average farm family raises a wide variety of livestock and poultry (SEA, 2010).

1.5.6 Hydrogeology

The Voltaian formation is characterized essentially by little or no primary porosity. Therefore, groundwater occurrences are associated with the occurrence of secondary porosities caused by fracturing, faulting, jointing and weathering (Yidana et al., 2007). Aquifers in the study area are generally semi-confined and structurally controlled and developed by secondary porosity in the form of fractures and primary porosity has been destroyed through compaction and slight metamorphism (Junner and Hirst, 1946; Bannerman, 1975; Dapaah-Siakwan and Gyau-Boakye, 2000). Acheampong and Hess (1998) also confirmed that the hydrogeological parameters in the study area are based on secondary permeability in the form of joints developed after the primary porosities had been destroyed by rock compaction and slight metamorphism and as result has led to relatively poor success of drilling in those aquifers.

The secondary porosity which results from jointing, shearing, fracturing and weathering has given rise to two main types of aquifers in the Voltaian; the weathered zone aquifer and the fractured zone aquifers. The weathered zone aquifers usually occur at the base of the thick weathered layer while the fractured zone aquifers usually occur at some depth beneath the weathered zone (Kortatsi, 1994). According to Wardrop and Associates (1980), analysis of the available hydrogeological and lithological data from wells drilled in the study area indicates that fractured aquifer provides most of the well with water.

The nature, aperture and degree of interconnection between joints determine the hydrogeological fortunes of the rocks. The structural grain is made of NNE–SSW fracture systems, which control the hydrogeological character of the Voltaian sedimentary rocks in general (Yidana et al., 2007).

Borehole yields within the fractured zone are determined by the extent and degree of fracturing and therefore a formation which combines a thick weathered zone with a well fractured bedrock zone may provide the most productive aquifer situation.

Within the Middle Voltaian formation, the success rate for drilling boreholes through is about 56%, and the borehole yield ranges between 0.41 m^3/h and 9 m^3/h with an average yield of about 6.2 m^3/h (Dapaah-Siakwan and Gyau-Boakye, 2000). The groundwater fortunes of this terrain have been extensively investigated (Wardrop and Associates, 1980; Kotatsi, 1994; Acheampong, 1998; Agyekum, 2004) and has been established that recharge to all the aquifer systems is mainly by direct infiltration of precipitation through fracture and fault zones along the highland fronts and also through the sandy portions of the weathered zone while some amount of recharge may also occur through seepage from ephemeral streams channels during rainy seasons.

Transmissivity is a fundamental property of aquifers and water-bearing materials. In homogeneous aquifers, transmissivity (T) is the product of hydraulic conductivity (K) and the saturated aquifer thickness (b), that is:

$$T = Kb \qquad \text{(Equation 1.1)}$$

The transmissivity within the formation ranges between 1 m^2/d and 71.6 m^2/d with an average of 15.9 m^2/d. The aquifer transmissivity among the sandstones is in the range of 0.1 m^2/d to 52.0 m^2/d, and in the siltstone and mudstone aquifers, transmissivity is in the range of 0.2 m^2/d to 16.0 m^2/d (Yidana et al., 2012).

The recharge rate computed in the Voltaian ranges between 2.07×10^{-5} m/day and 2.85×10^{-4} m/day which is about 0.3% to 4.1% of the annual precipitation in the area (Yidana et al., 2012)

CHAPTER TWO

LITERAURE REVIEW

2.1 Groundwater Recharge

Recharge has been defined as “the entry into the saturated zone of water made available at the water-table surface, together with the associated flow away from the water table within the saturated zone” (Freeze and Cherry, 1979). It is the process by which groundwater is replenished. Groundwater can be recharged both by precipitation moving down through the soil and rock layers of the ground and by infiltration from surface water sources such as rivers and lakes (GWRPH, 1986; Bhattacharya et al., 2003).

Groundwater recharge is described by Sophocleous (2004) as a hydrologic process which is an endless circulation of water as it moves in its various phases through the atmosphere, to the Earth, over and through the land, to the ocean, and back to the atmosphere. The process is powered by the sun; through phase changes of water (i.e. evaporation and condensation) involving storage and release of latent heat (Sophocleous, 2004). Precipitation is delivered to streams on the land surface as overland flow to tributary, channels, and in the subsurface as interflow or lateral subsurface flow and base flow following infiltration into the soil (Sophocleous, 2004).

Ng et al. (2009) established that the primary controls on recharge are meteorology, soil properties, vegetation, and topography and these controls interact to create the distinctive conditions that result in recharge. The uncertainties associated with the control mechanisms make it difficult to predict long-term effects of climatic change, meteorological variability, and land use change on groundwater resources.

De Vries and Simmers (2002), categorized recharge as ‘‘diffuse’’ (or ‘‘direct’’) when it originates from precipitation that infiltrates vertically from the surface directly to the water table. In contrast, non-diffuse (‘‘localized’’ or ‘‘focused’’) recharge travels laterally at (or near) the land surface and then collects in streams or topographic depressions before it infiltrates. Both diffuse and localized recharge often travels via preferential pathways, such as through cracks or root tubules, rather than exclusively through the soil matrix. Preferential flow is especially difficult to characterize or predict. Kearns and Hendrickx (1998), point out that small amount of diffuse recharge spread over a large area can yield significant volumetric contributions to groundwater in semiarid regions of New Mexico. Also, in areas where deep-rooted vegetation has been replaced by shallow-rooted crops or pasture, diffuse recharge rates can increase significantly (e.g., Cook et al., 1989; Scanlon et al., 2007).

Understanding of the downward moisture movement driven by precipitation and upward moisture movement driven by evapotranspiration and root uptake is very relevant in groundwater recharge (Ng et al., 2009). Groundwater recharge identification and quantity is very critical in its managements and so Mazor (2004) outlined certain features characterizing recharge regions including:

- Depth of water table is at least a few meters below the surface.
- Water table contours show a local high.
- Significant seasonal water table variation are noticed
- Local groundwater temperatures are equal to, or several degrees colder than, the average ambient annual temperature.

- Effective water ages are very recent (a few months to a few years).
- Salt content is low in most cases in non-polluted areas (less than about 800 mg/L total dissolved ions).
- Surface is covered by sand, permeable soil, or outcrops of permeable rocks.

2.2 Groundwater Recharge Estimation

Estimating groundwater recharge in arid and semi-arid regions can be difficult, since in such areas the recharge is generally low compared to the average annual rainfall or evapotranspiration, and thus making it difficult to quantify precisely (Scanlon et al., 2002; Beekman, 1996). Different methods can be used to estimate groundwater recharge, such as empirical approaches, water-balance techniques, the Darcy law in unsaturated zones, tracer techniques and others depending on data availability and the field situation (Eagelson, 1979; Lerner et al., 1990; Flint et al., 2002; Edmunds et al., 2002). Environmental isotopes and chloride – mass balance (CMB) have commonly been used in water resource development and management (Fritz and Fronte, 1980; Subyani, 2004). Xu and Beekman (2003) reviewed literatures on recharge estimation methods used in a number of southern African countries including Botswana, Zimbabwe, Namibia and South Africa and came up with a list of commonly used methods. The list indicates that the chloride mass balance, cumulative rainfall departure, extended model for aquifer recharge and moisture transport through unsaturated hard rock, water table fluctuation, groundwater dating and modeling, historical tracers (e.g., 3H) and the zero flux plane have often been used with high accuracy in the Southern African countries.

Numerical models are very useful in groundwater recharge estimation but many studies (Allison et al., 1994; Phillips, 1994; Gee and Hillel, 1998) have cautioned against its application in semiarid environment. Because diffuse recharge rates in such settings can be quite small relative to precipitation and evaporation, they are very sensitive to uncertain model parameterizations and input errors. For this reason, tracer-based recharge estimation methods are favored by Allison et al. (1994) and Gee and Hillel (1988) 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).

Accurate quantification of recharge rates is imperative to proper management and protection of valuable groundwater resources. For proper management systems the recharge to the aquifer cannot be easily measured directly but usually estimated by indirect means (Lerner, 1990). The accuracy of the indirect estimation is also usually difficult to determine, and therefore it is recommended that recharge should be estimated using multiple methods to obtain more reliable values (Lerner, 1990; Scanlon et al., 2002).

2.3 Chloride Mass-Balance

The chloride mass balance (CMB) was first put forward by Eriksson & Khunakasem (1969), and is based on the mass conservation to estimate groundwater recharge. Chloride is assumed to be conservative based a history of use as a tracer. 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 chloride-mass balance method is applied to estimate the recharge flux for most aquifers by using the best possible values of the three measured components, i.e., effective rainfall, chloride concentrations in rainfalls, and groundwater (Subyani, 2004). The chloride-mass balance method has been used to estimate recharge in arid and semiarid regions throughout the world (Allison et al., 1994; Prych 1995; Murphy et al., 1996; Hendrickx and Walker 1997; Scanlon, 2000).

The CMB method appears to be useful in estimating paleoclimate recharge rate dating back thousands of years (Murphy et al., 1996; Tyler et al., 1996), but CMB has also been used for estimating modern recharge rates, including those that have increased in response to land-use change, specifically where vegetation had been altered and deep-rooted trees were replaced with shallow-rooted grasses (Jolly et al., 1989; Walker et al., 1991). A direct method of calculating the mass flux of water reaching the water table using four parameters are chloride content in precipitation (Cl_p), chloride content in groundwater (Cl_{gw}), Average annual precipitation (P), recharge (R) which is given by the following equation (2.1) (Allison and Hughes, 1978);

$$R = P\frac{Cl_p}{Cl_{gw}} \qquad (2.1)$$

Chloride is the most widely used environmental tracer and originates in precipitation and dry fallout and is transported into the subsurface with infiltrating water. Chloride concentrations in unsaturated zone pore water are inversely related to recharge: 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.

This method of groundwater recharge estimation can be useful when the following assumptions made by Zhu (2003) are considered; thus, if it can be assumed that; (1) atmospheric deposition is the only source for Cl^- in groundwater, (2) Cl^- behaves as a conservative tracer along its path, (3) Cl^- uptake by roots and anion exclusions are negligible, (4) leaching of Cl^- deposit at ground surface and in the soil zone is complete, (5) groundwater movement in both unsaturated zone and saturated zone can be approximated as one-dimensional piston flow, and (6) surface run-on and runoff can be neglected, then the Cl^- concentration of groundwater recharge is a result of evapotranspiration (ET) loss of water.

2.4 Water Table Fluctuation

The water table is the surface where the water pressure head is equal to the atmospheric pressure. It may be conveniently visualized as the 'surface' of the subsurface materials that are saturated with groundwater in a given area (Sophocleous, 2004). Water-level monitoring is an essential component of field studies associated with the analysis of artificial recharge. According to Sophocleous (2004), the main techniques used to estimate ground water recharge rates can be divided into physical methods and chemical methods (Allison, 1988; Foster, 1988). Among the physical methods, the water table fluctuation technique (WTF) links the change in ground water storage with resulting water table fluctuations through the storage parameter (specific yield in unconfined aquifer). This method is considered to be one of the most promising and attractive due to its accuracy, ease of use and low cost of application in semiarid areas (Beekman and Xu, 2003).Water-level fluctuations can result from a wide variety of hydrologic phenomenon, some natural and some induced by man. There are so many techniques which can be applied in groundwater estimation but Water Table Fluctuation is among the most widely-applied methods for estimating recharge rates. This is likely due to the abundance of available groundwater-level data and the simplicity of estimating recharge rates from temporal fluctuations or spatial patterns of groundwater levels. It only requires knowledge of specific yield and changes in water levels over time.

The WTF method is based on the assumption that rises in groundwater levels in unconfined aquifers are due to recharge water arriving at the water table and is best applied to aquifer systems with shallow groundwater levels showing quick responses to precipitation events (Healy and Cook, 2002; Scanlon et al., 2002; Moon et al., 2004). Water-table fluctuations (WTF) were used to estimate recharge from the water-level rise in a well multiplied by the specific yield of the aquifer (Rasmussen and Andreasen, 1959). This method actually measures the effect of recharge at the water table, so it should provide estimates that correspond most closely to our definition of recharge; however, the appropriate value of specific yield must be known to translate the measured water-level fluctuations into estimates of recharge (Risser et al., 2005).

Specific yield, $S_{y,}$ is defined by Freeze and Cherry (1979) as the volume of water that an unconfined aquifer releases from storage per unit surface area of an aquifer per unit decline in the water table. Specific yield of an aquifer can either be determined using the laboratory method or the aquifer test approach. The laboratory method determines specific yield base on porosity and specific retention (Johnson et al., 1967). Values of Sy and transmissivity, T, for unconfined aquifers are commonly obtained from the analysis of aquifer tests conducted over a period of hours or days. Drawdown- versus-time data from observation wells are matched against theoretical type curves developed using the aquifer test approach (Boulton, 1963; Prickett, 1965; Neuman, 1972; and Moench (1995, 1996).

Specific yield of an aquifer varies with texture of aquifer materials, Table 2.1 shows the variation. This method has been used by many scientists to estimate groundwater recharge. A detailed account is given by (Healy and Cook, 2002; Shirahatti et al., 2012; Hall and Risser, 1993). Moon et al. (2004) suggested a modified WTF method estimating groundwater recharge using the product of specific yield and the ratio of water-level rise over the cumulative precipitation. They applied the modified method to water level data obtained from the National Groundwater Monitoring Network of Korea and evaluated the spatial variability of recharge in river basins whose distances are at least over 20 km.

The WTF technique has some advantages in the sense of its simplicity and insensitivity to the mechanisms by which water moves through the unsaturated zone.

Table 2.1: Statistics on specific yield from 17 studies compiled by Johnson (1967)

Texture	Average specific yield	Coefficient of variation (%)	Minimum specific yield	Maximum Specific yield	Number of determinations
Clay	0.02	59	0	0.05	15
Silt	0.08	60	0.03	0.19	16
Sandy clay	0.07	44	0.03	0.12	12
Find sand	0.21	32	0.1	0.28	17
Medium sand	0.26	18	0.15	0.32	17
Coarse sand	0.27	18	0.2	0.35	17
Gravelly sand	0.25	21	0.2	0.35	15
Fine gravel	0.25	18	0.21	0.35	17
Medium gravel	0.23	14	0.13	0.26	14
Coarse gravel	0.22	20	0.12	0.26	13

However, difficulties in applying the method as describe by Shirahatti et al. (2012) are related to determining a representative value for specific yield and ensuring that fluctuating in water levels are due to recharge and are not the result of changes in atmospheric pressure, the presence of entrapped air, or other phenomena, such as pumping. This method used in groundwater estimation has its own limitation as outlined by Healy and Cooks, (2002);

1. The method is best applied to shallow water tables that display sharp water-level rises and decline. Deep aquifers may not display sharp rises because wetting fronts tend to disperse over long distances. Nonetheless, the method has been applied to systems with thick unsaturated zones that display only seasonal water level fluctuations.
2. Typically, recharge rates vary substantially within a basin, owing to differences in elevation, geology, land surface slope, vegetation, and other factors. Wells should be located such that the monitored water levels are representative of the catchment as a whole.
3. The method cannot account for a steady rate of recharge. For example, if the rate of recharge were constant and equal to the rate of drainage away from the water table, water levels would not change and the WTF method would predict no recharge.
4. Other difficulties relate to identifying the cause of water-level fluctuations and calculating a value for specific yield (Beekman and Xu, 2003).

2.5 Environmental Isotope Tracers

Environmental isotopes applied most often in waters and dissolved solids include the stable isotopes ^{13}C, ^{18}O, ^{2}H, ^{34}S, ^{15}N, and the radioactive isotopes ^{3}H, ^{14}C, ^{87}Sr, ^{36}Cl, and U disequilbrium. Uranium disequilbrium includes the large progeny of decay schemes for the parents 238U, 235U, and 232Th (Ivanovich and Harmon, 1992). Environmental isotope tracers are present in the Earth's atmosphere and are used to estimate recharge rates and evaluate system response to land use/land cover change and paleoclimate. Useful environmental tracers include; common dissolved constituents, such as major cation and anions; stable isotopes of oxygen (^{18}O) and hydrogen (^{2}H) in water molecules; radioactive isotopes such as tritium (^{3}H) and radon (^{222}Rn), and water temperature. The entire measurements and interpretations of environmental isotopes are predicated on isotopes occurring naturally in the hydrosphere, originating from cosmogenic nuclide production, or occur as persistent anthropogenic releases into the hydrosphere but not “manually” injected in to the environment as may be perceived.

Isotopic tracers use for subsurface hydrogeology is significant because of the innate difficulty of imaging subsurface processes with traditional hydrometric tools. However, it is possible to utilize isotopes because of its conservative nature (Tyler et al., 2000; Herczeg and Edmunds, 2000; Uemura et al., 2012);

- to trace groundwater flow paths,
- to estimate solute exchange from one phase of a system to another
- to determining extents of chemicals reactions in the subsurface
- for identifying source regions in watersheds
- for identifying recharge areas of aquifers
- for estimating subsurface residence times.

Salem et al. (2004) in their paper used subsurface temperature, stable isotopes and water quality to determine the pattern and spatial extent of groundwater flow at Nagaoka area in Japan. The log of TDS (mg/L) and $\delta^{2}H$ (‰) plot were used to shows the major forms of recharge in Lockyer Valley, Queensland, Australia and the recharge were identified as directly from streams and indirectly from basalts, and from sandstone bedrock (Cox and Wilson, 2005). The difference in concentrations of environmental tracers between groundwater and surface water can be used to identify and delineate zones of groundwater discharge or recharge, provided that the differences are sufficiently large (Kalbus et al., 2006).

The application of environmental isotope techniques has played an important role in solving the envisaged hydrogeological problems that cannot be solved by conventional method alone. Verhagen et al. (1991), confirmed that application of these techniques in the case of arid and semi – arid zones, where the available water resources are often limited to groundwater, has proved to be an attractive tool for the identification of paleogroundwater and the quantitative evaluation of groundwater system. (IAEA, 1980; 1983). Geochemical tracers, such as major chemical parameters (e.g., sodium, nitrate, silica, and conductivity) and trace elements (e.g. strontium), are often used to determine the fractions of water flowing along different subsurface flowpaths (Kalbus et al., 2006). Stable isotope tracers, such as oxygen and hydrogen isotopes, are used to distinguish rainfall event flow from pre-event flow, because rain water often has a different isotopic composition than water already in the catchment (Kendall and Caldwell, 1998).

2.6 Hydrogen and Oxygen Isotopes

Water isotope hydrology addresses the application of the isotopes that form water molecules. These are the oxygen isotopes (^{16}O, ^{17}O, ^{18}O) and the hydrogen isotopes (^{1}H, ^{2}H, ^{3}H). These isotopes are ideal tracers of water sources and movement because they are constituents of water molecules. They are not dissolved in water like other tracers of 'water' such as Cl^- which still is widely used as a tracer. These elements (hydrogen, oxygen) undergo changes in the various hydrologic environments i.e. atmosphere, hydrosphere, biosphere and the upper part of the earth's crust. The main processes that dictate the oxygen and hydrogen isotopic compositions of waters in a catchment are:

(1) phase changes that affect the water near the ground surface (i.e. evaporation, condensation, melting); and

(2) simple mixing at or below the surface.

Faure (1986) also stated that heavy isotope fractionation is affected by various processes such as altitude, biological, condensation, chemical, evaporation, freezing, melting and evapotranspiration. These phase changes result in isotopic fractionation which is the separation of element into lighter and heavy fractions. There are two stable isotopes of hydrogen, ^{1}H and ^{2}H (deuterium), as well as three stable isotopes of oxygen, ^{16}O, ^{17}O, and ^{18}O (Fetter, 1994). There are nine different combinations of these isotopes that make stable water molecules with atomic masses ranging from 18 to 22. The most abundant water molecule, $^{1}H_2{}^{16}O$, which is the lightest, has a much higher vapor pressure than the heavier form $^{2}H_2{}^{18}O$. During phase changes of water between liquid and gas the heavier water molecules tend to concentrate in the liquid phase, which fractionates the hydrogen and oxygen isotopes (Fetter, 1994). For instance water that evaporates from the ocean is isotopically lighter than the water remaining behind, and precipitation is isotopically heavier; that is it contains more ^{2}H and ^{18}O than the vapor left behind in the atmosphere.

The deuterium D to hydrogen H isotope ratio: D/H, as well as the O^{18} isotope to O^{16} isotope ratio, O^{18}/O^{16} are usually expressed as the dimensionless δ values, which is 'per thousand' or 'per mille' deviation of the isotope ratio from an internationally accepted standard (Craig 1961):

$$\delta(‰) = \frac{R_{sample-} \ R_{V-SMOW}}{R_{V-SMOW}} \ X \ 1000 \qquad (2.2)$$

where; R = D^2/H^1 or O^{18}/O^{16}. The reference standard used is called the Vienna Standard Mean Ocean Water (V-SMOW). Positive values of $\delta^{18}O$ and δD indicate enrichment of the sample in $\delta^{18}O$ as compared to SMOW, whereas depletion reflects negative values of $\delta^{18}O$ and δD in the relative to the standard.

Stable isotope ratio measurements of oxygen ($^{18}O/^{16}O$) and hydrogen ($^{2}H/^{1}H$) ratio in water which is used to compare the isotopic character of different waters lies in the use of δD - $\delta^{18}O$ plot of the isotope ratios. The plot of δD ‰ V-SMOW versus $\delta^{18}O$ ‰ V-SMOW is used to demonstrate the position of all samples relative to the Global Meteoric Water Line (Craig 1961). Base on about 400 water samples of river, lakes, and precipitation from various countries, an impressive lining of the data along best-fit line has been obtained called Global meteoric water line (Craig, 1961);

$$\delta D = 8 \ \delta^{18}O + 10 \qquad (2.3)$$

Meteoric line is a convenient reference line for the understanding and tracing of local groundwater origins and movements. Hence, in each hydrochemical investigation the local meteoric line has to be established from samples of individual rain events or monthly means precipitation (Mazor, 2004). The Global meteoric water line and the local meteoric water line are used as a reference line. When plotted rainwater samples fall below the meteoric water line, it’s reflect secondary fractionation by evaporation prior to infiltration, or the presence of ancient waters that originated in a different climate regime (Fritz et al., 1979). If the compositions of the groundwater plots are found on the local meteoric line or very close to it, then it rules out secondary processes such as evaporation prior to infiltration or isotope exchange with aquifer rocks (Mazor, 2004).

Stable isotope of oxygen and deuterium has a wide variety of usage in groundwater resource management. It can be used as sensitive tracer and widely used in studying the natural water circulation and groundwater movement (Subyani, 2004). Rapti-Caputo and Martinelli (2008) also used stable isotopes of oxygen and Deuterium to identify mixing phenomena between unconfined and confined aquifer system and evaluate the mean residence time of groundwater within the reservoirs of Ferrara area.

2.7 Deuterium Excess in Precipitation

Systematic study of variations in the isotopic ratios of oxygen and hydrogen in various components of the water cycle is helpful for understanding local and regional hydro-climatology. The relationship between the isotopic ratios of oxygen and hydrogen in precipitation is defined as the Meteoric Water Line (MWL) which yields valuable information about the climatic factors and secondary moisture sources which influence the precipitation process, when compared with global MWL.

The deuterium excess (or d-excess) is defined by (Dansgard, 1964) as;

$$d(‰) = \delta D - 8 * \delta^{18}O \qquad (2.4)$$

where δD and $\delta^{18}O$ are deuterium and oxygen-18 composition of water, respectively, has shown specific potential in the climate studies for tracing past and present precipitation processes (Froehlich et al., 2002).

D-excess as described by Froehlich et al. (2002), is a measure of the relative proportions of ^{18}O and ^{2}H contained in the water, and can be visually depicted as an index of deviation from the global meteoric water line (MWL; d=10) in $\delta^{18}O$ versus $\delta^{2}H$. D-excess correlate with the physical condition (humidity, air temperature and sea surface temperature) of the oceanic source at the area of the precipitation (Merlivat and Jouzel, 1979). Decreases in d-excess value below zero per mil are observed at stations with high temperature and/ or low vapour pressure (eg. Mali, Chad, Venezuela) where kinetic isotopic fractionation processes, connected with partial evaporation of the raindrops (Stewart, 1974), affects the d-excess of the collected precipitation. Partial evaporation of the precipitation sample during the storage in the rain gauge under warm and dry atmospheric condition may also lead to a decrease in d-excess (Froehlich et al., 2002).

The enrichment of heavy isotopes in rain water is primarily controlled by rain re-evaporation (raindrops get more enriched as they re-evaporate), diffusive exchanges and the recycling of the boundary vapour by depleted vapour from convective downdrought generated by the rain re-evaporation (Risi et al., 2008). The isotopic signature of precipitation may also be controlled by (1) the origin of the air masses, (2) rain re-evaporation (Barras and Simmonds, 2009), (3) condensation altitude, at higher condensation altitude, the vapour is more depleted due to previous condensation and thus the condensate forming the precipitation is more depleted (Celle-Jeanton et al., 2004) and (4) diffusive exchanges between the low-level vapour and the raindrops that deplete the vapour (particularly efficient when the relative humidity is high: Gedzelman et al., 2003; Fudeyasu et al., 2008). D-excess has been used to infer and identify the origin of subsurface ice or derive evidence of secondary processes (Meyer et al., 2002; Stenni et al., 2007; Fisher et al., 2004).

CHAPTER THREE

METHODS AND MATERIALS

3.1 Sample Collection and Analysis

Water samples were collected in the month of December, 2012. The samples were taken from different sources of water which included groundwater and surface water within the study area. To give a good representation of samples collected from a large district like Gushiegu, which is about 5796 km^2 (SEA, 2010), two or more samples were picked to represent a community in the district, to ensure even distribution of data as much as possible. A total of 53 water samples were collected; at various locations (Fig. 3.3) 28 from boreholes (Fig. 3.1), 13 from surface water (small rivers and dams) (Fig. 3.2) and 12 from rain water, following standard protocols described by USGS (2006), and Duncan et al. (2007). In sampling from the hand pumps, purging was done for ten (10) minutes to flush the stagnant water retained in pipes. In the case of hand dug wells, it was properly checked and confirmed that the hand dug well was being used daily. This was to ensure that stale and stagnant water was not sampled.

Samples were also taken from two "Special wells" (Fig. 3.4), identified at the area and was informed there are more of such wells in the study area. The "Special well" herein is identified as SP is a well which was found in the course of data collection and is believed not to have been dug by the community but has been there for ages. The indigenous people of the area believe the well was made by the gods in ancient time to supply their ancestor with water, since the area has no major surface water and they have also come to enjoy its benefits.

Figure 3.1: Photograph showing some of the sampled bore holes

Figure 3.2: Photograph showing some of the sampled surface water (dam)

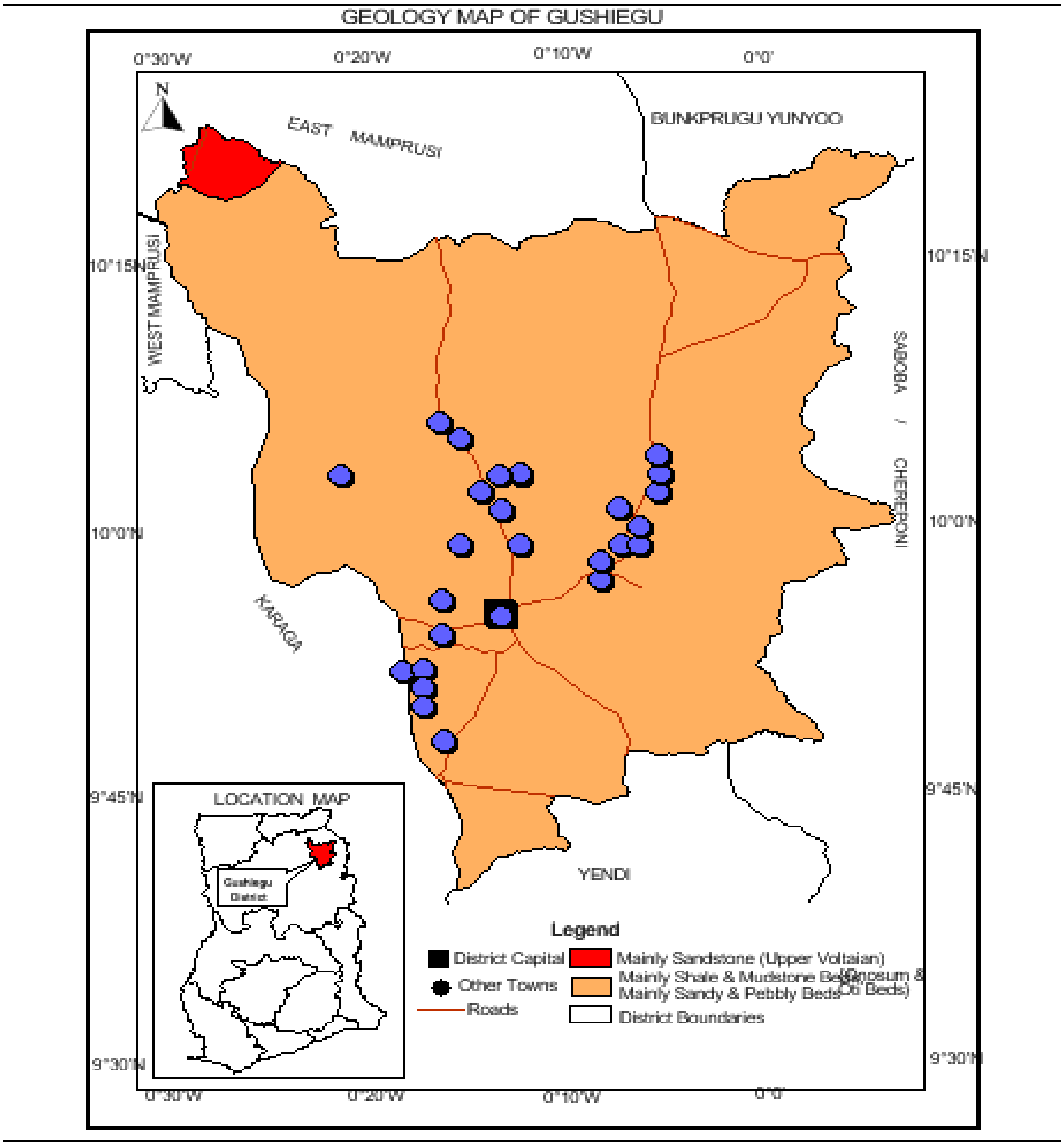


Figure 3.3: Geological map of study area showing sampling points.

As shown in Figure 3.4, the SP is an “envelope” of rocks containing water with a narrow hole at the top from which water can be fetched. The people went further to explain that the SP becomes more recharge during the rainy season.

Figure 3.4: A photograph showing one of the “special wells” identified.

Three samples were collected at each site into 500 mL pre-sterilized polyethylene bottles. Filled bottles at each location were labeled cation, anion and isotopes. Samples labeled cations were immediately acidified by the addition of nitric acid. The filled bottles labeled anion and cation were stored in an ice chest with ice of temperatures below 4^{o}C. This is to ensure that the chemical composition of the sampled water is not altered. The bottles labeled isotope were stored in ice chests without ice and kept way from sunlight to prevent alteration of the isotopic composition of the samples due to fractionation from sunlight and glacier. The samples were transported to the National Nuclear Research Institute (NNRI) of the Ghana Atomic Energy Commission’s chemistry laboratory and stored at temperature below 4 ^{o}C until they were all analyzed. 12 rain water samples were also collected during the rainy season into 500 ml polyethylene bottles at Tamale.

The samples were filtered with a white 0.45 µm membrane place in a filter holder. A potable EC meter (Hach Sension 5) were used to measure some field parameters like TDS, Salinity and electrical conductivity and potable pH meter (Hach sension 1) were also used to measure pH and redox potential. Bicarbonate determination was also carried out in the laboratory using double-indicator titration of 25 ml sample against 0.01M HCl, with phenolphthalein and methyl orange as the indicator (Eaton et al., 2005).

Sodium and potassium were analyzed using Flame Emission Photometer. (Sherwood Model 420). Anions such as nitrates (NO_3^-), phosphate (PO_4^{3-}), sulphates (SO_4^{2-}) were analysed using Brucine reagent, Ascorbic Acid and Turbidimetric methods respectively and Ultra Violet Spectrometer (UV- 1201). Fluoride (F-) concentrations were obtained with the use of Hach Colorimeter (DR/890) (Franson et al., 1995). Magnesium (Mg^{2+}) and calcium (Ca^{2+}) were analyzed using digestion, followed by atomic spectrometry using the AA240S Fast Sequential Atomic Absorption Spectrometer (Franson et al., 1995; Sood et al., 2004; Eaton et al., 2005).

The Liquid Water Isotope Analyzer (LWIA) was used to analyze stable isotopes ($\delta^{18}O$ and $\delta^{2}H$). The stable isotope values were expressed in the conventional “delta’’ (δ) notation, which is measured in per mil from the international SMOW (Standard Mean Ocean Water) as shown in equation 2.2 (Négrel, 2007).

3.2 Determination of Sodium and Potassium

Sodium and potassium were analyzed using Flame Emission Photometer. The amount of potassium in the water samples was determined in a direct-reading type of flame photometer at a wavelength of 766.5 nm whilst the concentrations of sodium were determined at a wavelength of 589 nm. The Flame Photometer was set base on the required element to be determined. A blank solution and standards were aspirated in to the flame photometer and a plot of standard curve of sodium/potassium concentration against intensity is obtained. The water sample is then aspirated into the flame and reading recorded. A calibration curve was prepared by plotting the emission intensities as a function of Na/K concentration. The concentration of Na/K in the unknown sample is determined by reading the concentration of the sample which corresponds to its emission intensity from the calibration curve (Skoog, 2007).

3.2.1 Digestion of Water Samples for Atomic Absorption Spectrometer (AAS) Analysis

The concentration of Magnesium and Calcium were determined by the AAS but prior to that the water samples were filtered and digested. For Magnesium, 1mol of the sample were pipette into a test tube and 9 ml of lanthanum solution were added as a suppressant to dissolve the magnesium ions in solution. The magnesium ions are now ready to be analyzed using the Atomic Absorption Spectrometer (AAS). To digest the water sample to determine the concentration of calcium, 5 ml of raw water sample were pipetted into a Teflon bombs or beaker in three replicate. 6 ml of 65 % of concentrated HNO_3 was added to dissolve the metal in solution, 3 ml of 35 % HCl and 0.25 % or five drops of H_2O_2 (Catalyst) was added to each vessel containing the sample. The beakers were swirled gently to mix well and fitted vertically into the microwave digester (lab station ETHOS 900) and digested for 20 minutes (Fisherman and Downs, 1966). Once digestion was completed, the solution containing the sample were cooled down in water bath for twenty (20) minutes 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. After the digestion process, the solutions were transferred into test tubes and were taken for AAS analysis. To ensure quality control and quality assurance blank samples were also digested along with each set of samples and subsequently analyzed for appropriate elements through the same procedure.

3.2.2 Atomic Absorption Spectrometry (AAS)

Atomic absorption exploits different radiation wavelengths absorbed by different atoms, thus every element emits characteristics radiation when excited. In their elemental form, metals will absorb ultraviolet light when they are excited by heat (Fisherman and Downs, 1966). The AAS instrument is able to identify particular element by focusing a beam of ultra violet light at a specific wavelength through a flame and onto a detector. The sample of interest is aspirated into flame and the metal present in the sample absorb some of the incident light, thus reducing its intensity. This amount of energy (wavelength) is specific to a particular electron transition of a particular element. Each wavelength corresponds to only one element. The extent to which radiation of a particular frequency is absorbed by an atomic vapour is a function of the path length through the vapour. It also depends on the concentration of the absorbing atoms in vapour. The AAS generally measures the change in intensity as the light pass through the sample and a computer data system converts the change in intensity into absorbance (Ferreira et al., 2007). As the concentration goes up, the absorbance goes up.

To ensure the efficiency of the AAS machine standards are used to calibrate the machine and blanks are also prepared for reading to check for contamination. Calibration curves were constructed by running standards of various concentrations on the ASS and observing the absorbencies. The samples were later tested and measured against this curve (Parker, 1963; Ferreira et al., 2007).

3.2.3 Quality Assurance/Quality Control (QA/QC)

Quality assurance (QA) refers to the policies, procedures and actions established to provide and maintain a degree of confidence in data integrity and accuracy. For a monitoring program to successfully meet its objectives, a rigorous and thorough program of checks, comparisons and communication must be implemented. In order to achieve consistent data collection, a QA system must be followed (Ibe and Kullenberg, 1995; EPA Guidelines, 2007). Quality control (QC) is a sample procedure intended to verify performance characteristics of a system. Water sampling quality control ensures that the monitoring data sufficiently represents the condition of the target waters when the sample was collected. Thus, any significant change in, or contamination to, the sample due to containers, handling and transportation is identified through the incorporation of QC samples (EPA Guidelines, 2007).

To produce an acceptable result, the following QA/QC guidelines were taken during sampling and analysis. The sampling containers were cleaned and dried for 3 days and later rinse with deionized water before use. Collected samples were labeled and recorded with the type, location, date and environmental characteristics especially the vegetation cover. To prevent deterioration all the collected samples were kept under the required conditions before transported to the laboratory. International Standards of required reagent and deionized water were used throughout at the laboratory. The instruments were calibrated with chemical standards solutions prepared from commercially available chemicals and validated with Standard Reference Materials (SRM) and Certified Reference Material (CRM). Most of the analyses were repeated to serve as a check on the output results and to reduce error.

3.3 Chloride Mass Balance

Chloride mass-balance method relies on the salt-balance and the salt-age equations. The salt-balance equation is used to determine groundwater recharge rates (Allison and Hughes, 1978) (Equation 3.1). Chloride concentration in the water samples (groundwater and precipitation) collected in the field was determined by laboratory analysis. An average of chloride concentration in groundwater Cl_{gw} and rainwater Cl_p were determined. The average precipitation value in mm/year for the study area was obtained from literature as 1000 mm/year (Yidana et al., 2012).

Assuming the only source of chloride entering the unconfined aquifer is rainwater and generally the chloride concentration in shallow well are consistently higher than rainwater. Therefore these concentrated values are a direct result of evapotranspiration occurring from the top of the water table. The amount of evapotranspiration is quantifiable by first calculating a concentration factor which the ratio chloride concentration in rainwater to chloride concentration at each well.

$$\text{Concentration factor} = \frac{\mathrm{Cl_r}}{\mathrm{Cl_g}} \tag{3.1}$$

Where, Cl_r is chloride in rainwater and Cl_g chloride in groundwater. The concentration factor was used to determine how much of the precipitation has actually been evaporated (Ritort, 2007).

3.4 Water Table Fluctuation

The water table fluctuation method may be the most widely used technique for estimating recharge; it requires knowledge of specific yield and changes in water levels over time.

For water table fluctuation analysis, depth to water table data was obtained from Water Resource Commission of Ghana, Accra. Data on two monitoring wells obtained are WVB 12 and WVB 13, located at Tinguri and Galiwei respectively. WVB 12 was drilled on March 15, 2002 with depth of about 51 m; the WVB 13 was also drilled on July 6, 2006 with depth of about 100 m. The data contain daily monitored depth to water for 4 consecutive years from 2006 – 2010 for WVB12 and two years 2006 and 2008 for WVB 12.

Healy and Cooks (2002) mentioned that the WTF method is based on the premise that rise in groundwater levels in unconfined aquifers are due to recharge water arriving at the water table. Recharge is calculated as:

$$R = S_y \, dh/dt \tag{3.2}$$

where S_y is specific yield, h is water-table height, and t is time. With this equation it is assumed that all water arriving at the water table goes immediately into storage and that all other factors like evapotranspiration, base flow, recharge from irrigation and streams into groundwater is negligible. For this study, it is difficult to estimate base flow and recharge form stream so these factors are neglected (Shirahatti et al., 2012). Recharge from irrigation is also dropped because from SEA (2010), there are no significant irrigational facilities in the study area.

To tabulate a total recharge estimate, dh is set equal to the difference between the peak of the rise and low point of the extrapolated antecedent recession curve at the time of the peak. The antecedent recession curve is the trace that the well hydrograph would have followed in the absence of the rise-producing precipitation (Healy and Cooks, 2002).

3.5 Measurement of stable isotopes D and ^{18}O

Water samples collected for isotope analysis were 50 with 28 boreholes, 10 surface water and 12 rain water. The stable isotope composition of the water and the standards were measured using Liquid Water Isotope Analyzer (LWIA). In-house standards were use with the samples placed in a vial with the help of a disposable pipette tip. The vials containing the standards and samples are labeled and placed in their proper position on the auto sampler tray. The tray and its content were placed on the auto sampler and then configured to run. Standards are measured before and after every five readings. One major precautions inculpated into the LWIA is de-ionized water starting and ending with the arrangement of the vial in the tray which ensure there is no contamination from one set of sample to other.

CHAPTER FOUR

RESULT AND DISCUSSION

4.1 Summary of Physico-Chemical Analysis

Generally, the physico-chemical parameters of the analyzed samples show a spatial variation in cations, anions, Eh, pH, TDS, and EC. All the samples with the exception of GH 40 have low total dissolved solids (TDS) and can therefore be termed as fresh water (Freeze and Cherry, 1979). The TDS concentration ranges from 24.2 mg/L to 1194 mg/L (Figure 4.1) and 17.2 mg/L to 134.1mg/L (Fig. 4.2) for groundwater and surface water respectively. It can be observed from the box plots (Figs. 4.1 and 4.2) that, there is significant variation in TDS concentration values between groundwater (mean TDS of 592.2 mg/L) and surface water (mean TDS of 57.9), with groundwater having slightly higher values than surface water. These values may be reasonable because in the Gushiegu District there are no major industrial activities from which their sewage may contaminate the surface water and increase the TDS and EC.

The possible source of TDS in the area may be as a result of agricultural and residential runoff and natural source such as leaves, silt, plankton and the geology of the area (Kortatsi and Jørgensen, 2001). Also TDS in groundwater is higher than surface water because the average velocity of groundwater is very slow and so can dissolve a lot of constituent compared to surface water which moves faster. The box and whiskers plots also show some spatial variation in the hydrochemistry of the groundwater and surface water but are outside the scope of this study.

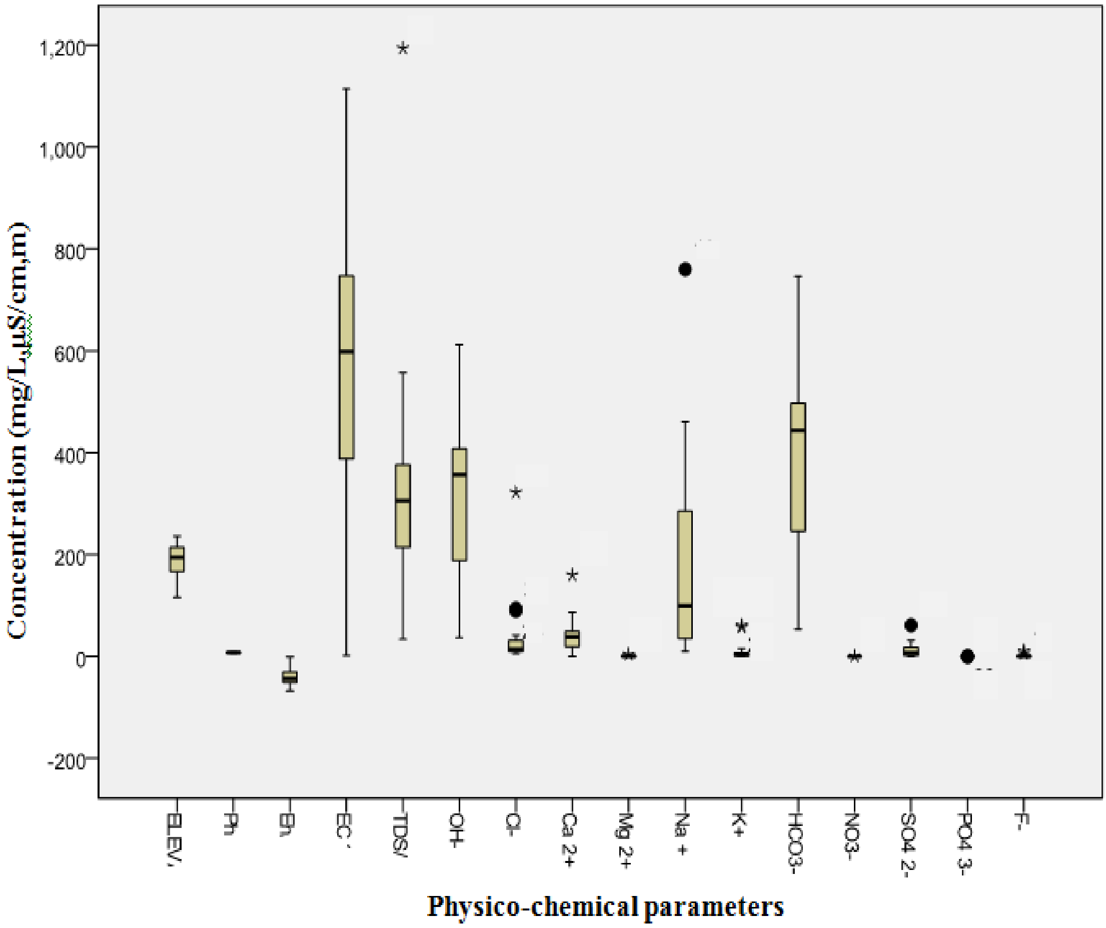


Figure 4.1: Box and Whiskers plot showing spatial variation in physico-chemical parameters of the groundwater.

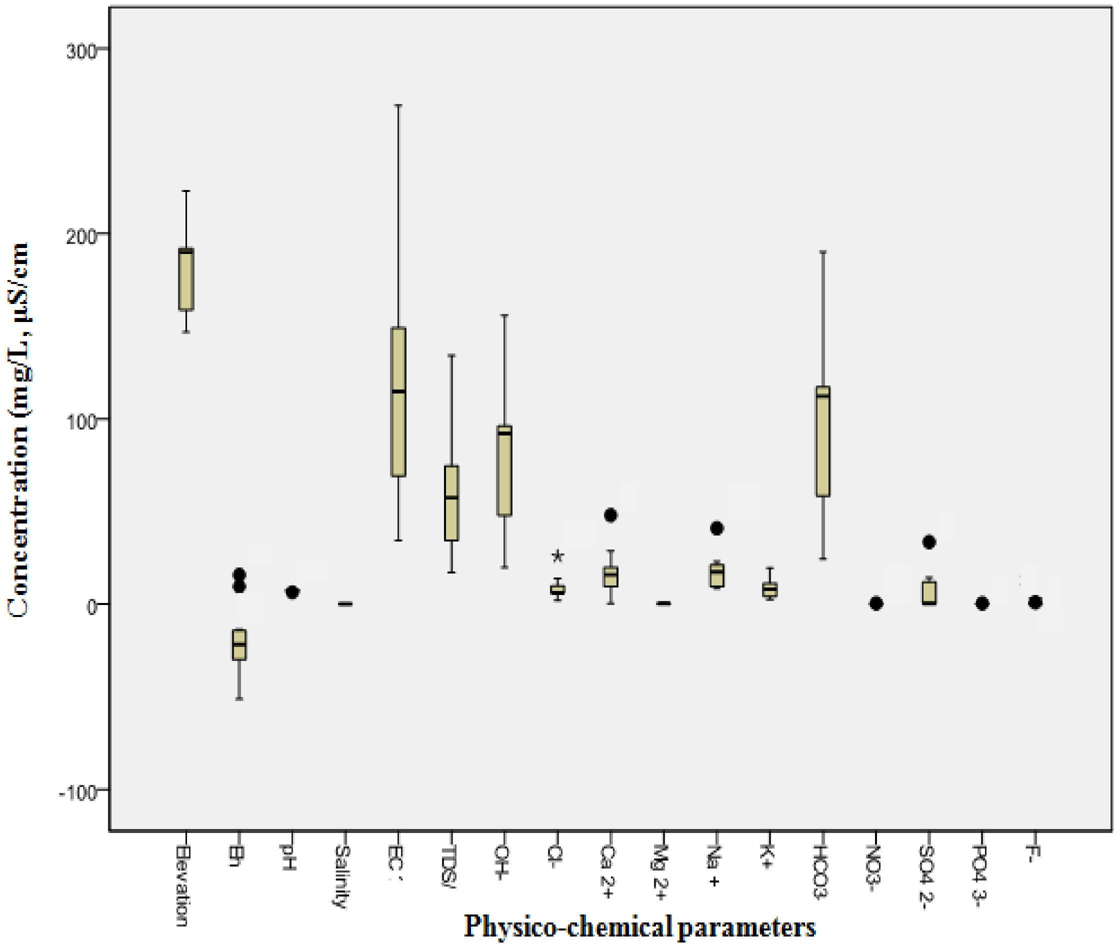


Figure 4.2: Box and Whiskers plot showing spatial variation in physico-chemical parameters of the Surface water.

4.1.1 Isotopes Results and Interpretations

The isotopic composition of water is expressed in comparison to the isotopic composition of ocean water. For this purpose an internationally accepted ocean water sample has been selected, called Standard Mean Ocean Water (SMOW) (Craig, 1961). The isotopic composition of water, determined by mass spectrometry, is expressed in per mil ‰ deviations from the SMOW standard. These deviations are written δD for the deuterium, and $\delta^{18}O$ as displayed in equation 2.2. Water with less deuterium than VSMOW has a negative δD; water with more deuterium than SMOW has a positive δD and the same is true for $\delta^{18}O$. The standards used to determine these values are given in Table 4.1, along with the associated laboratory errors for the procedure as describe above.

Table 4.1: The error for isotopic analysis, V-SMOW is Vienna –Standard Mean Ocean Water.

Element	**Standard**	**Error**
δD(water)	V-SMOW	±1.0‰
$\delta^{18}O$(water)	V-SMOW	±0.5‰

The box plots of water isotopes of $\delta^{18}O$, δD and d-excess are presented in Figures 4.3, 4.4 and 4.5 for surface water, groundwater and rainwater respectively. The inspection of the box plots for the δD and $\delta^{18}O$ of the groundwater is generally symmetrical with a range of -33.3 ‰ to -7.5 ‰ for δD and -5.1 ‰ to -1.8 ‰ for $\delta^{18}O$ and a mean of -21 ‰ and -3.8 ‰ respectively. The surface water isotopic data for $\delta^{18}O$ and δD is also generally non-skewed with a range of -11.6 ‰ to 20.3 ‰ for δD and -1.9 ‰ to 3.5 ‰ for $\delta^{18}O$. D-excess values for all the waters are skewed; for surface water it is skewed to relatively higher d-excess values while groundwater is skewed to relatively lower values. The rainwater values are also relatively skewed to the lower values (Fig. 4.5).

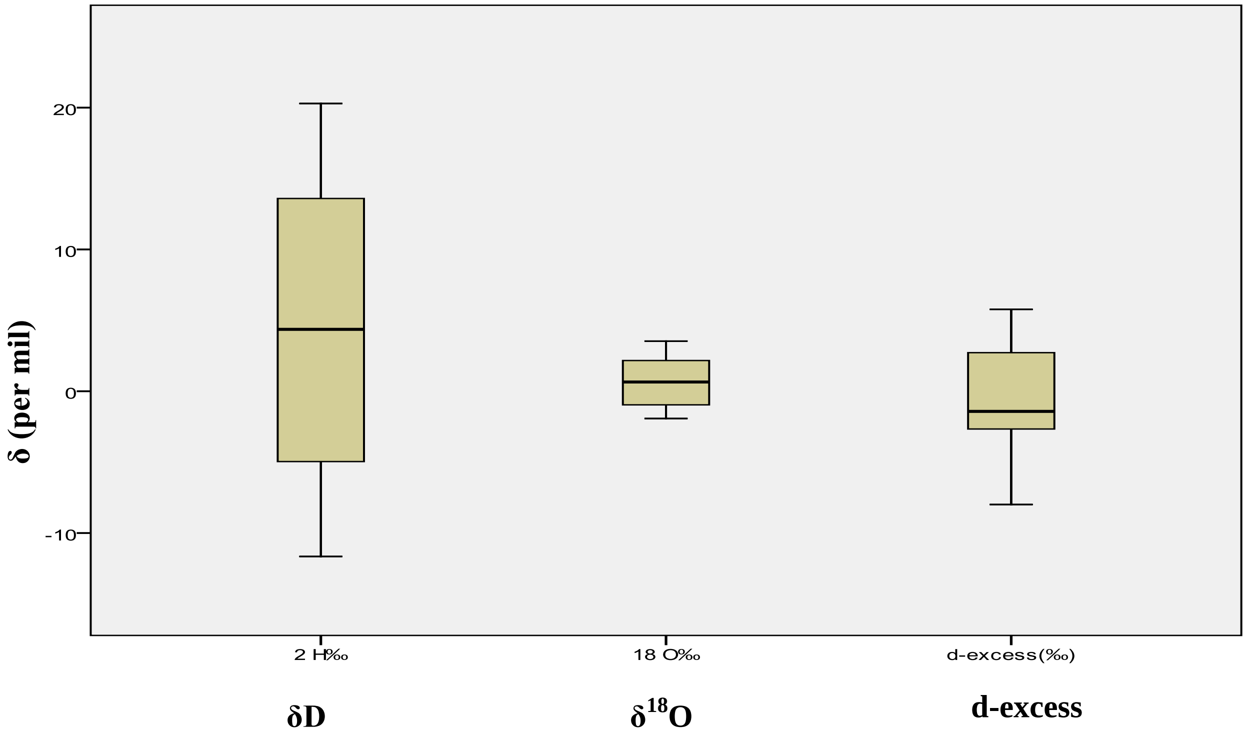


Figure 4.3: Box and Whiskers plots showing the spatial isotopic variation of the surface water.

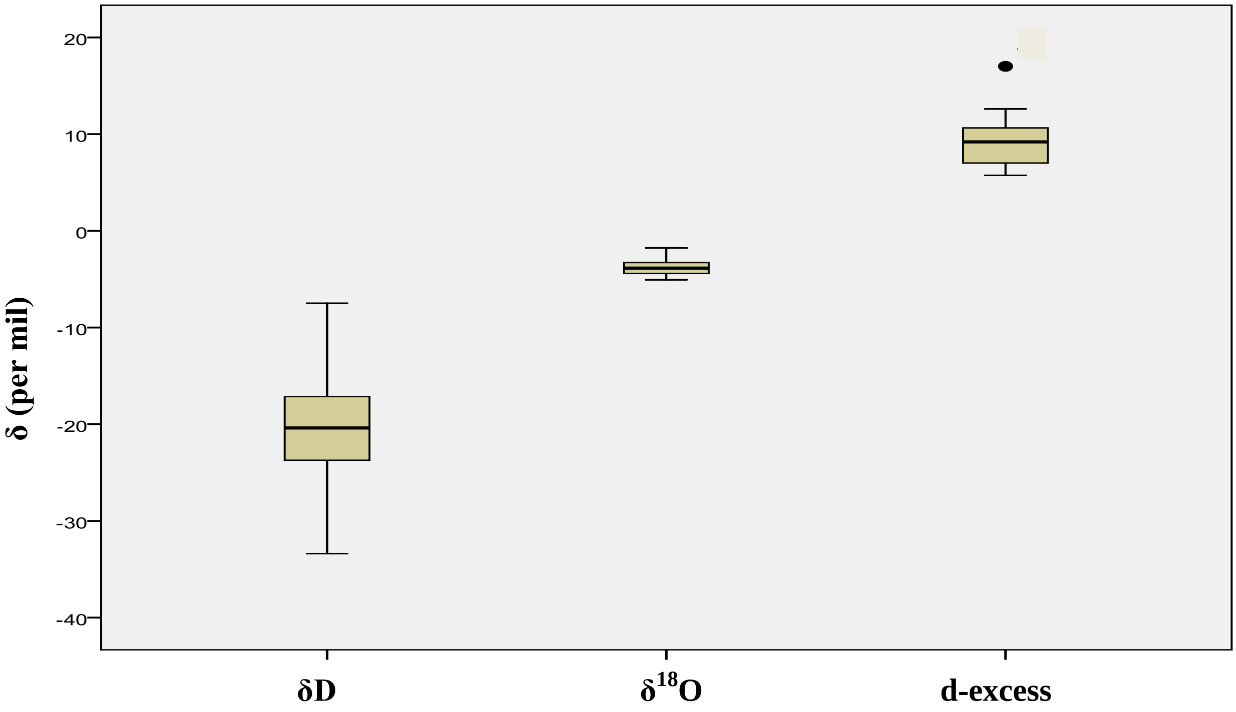


Figure 4.4: Box and Whiskers plots showing the spatial isotopic variation of the groundwater

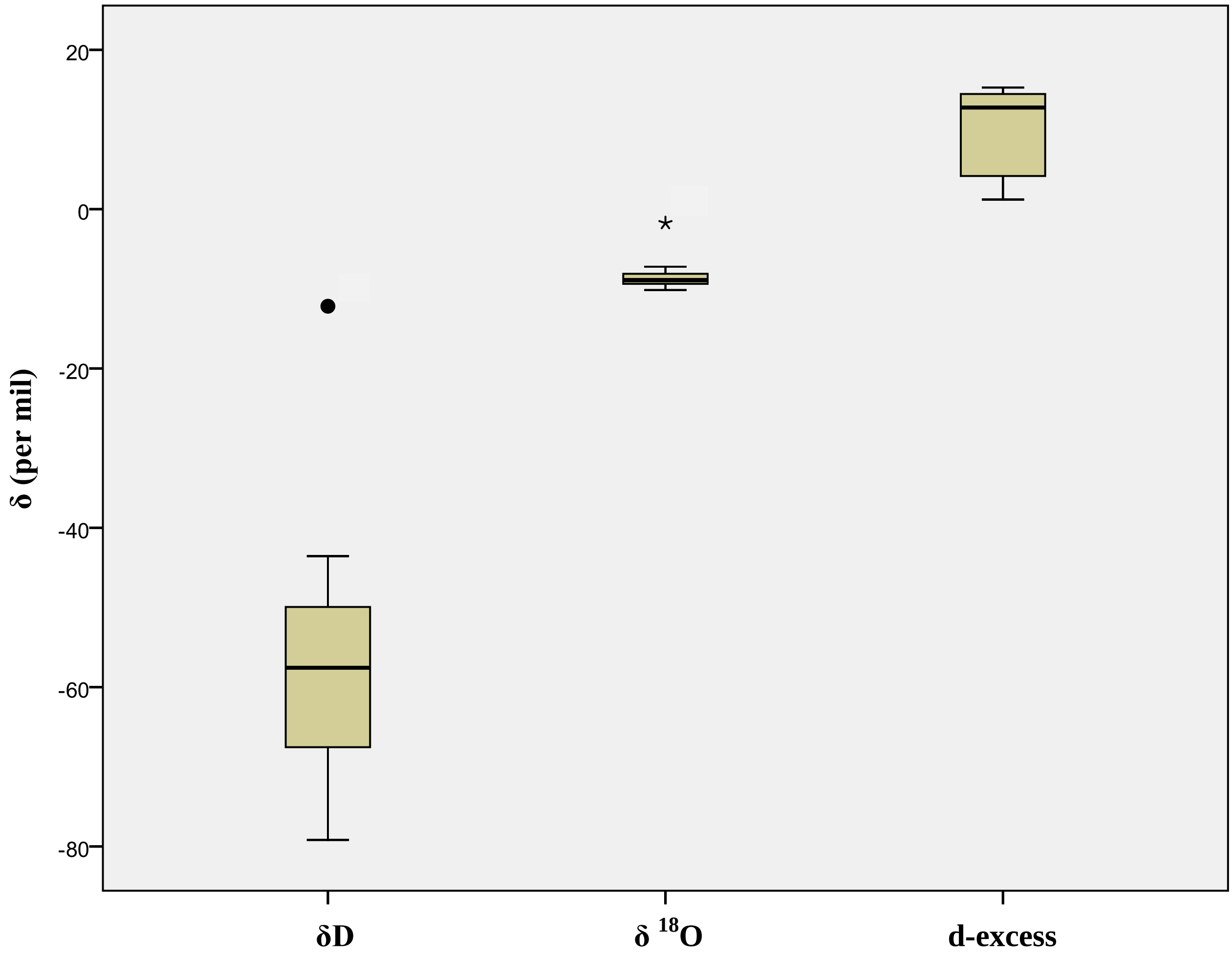


Figure 4.5: Box and whiskers plots showing variation in rainwater isotopic data.

The plots of δD vs. δ^{18}O were used to determine the factors that are controlling the interaction of surface water, groundwater and rain water of the study area. Craig (1961) defined a global meteoric water line (GMWL) as in equation 2.3. Where D and ^{18}O are heavy isotopes of oxygen and hydrogen respectively and δ is the isotopic enrichment parameter. This equation is the line of best-fit of plots made by Craig (1961) representing the global waters and might differ from the local meteoric water line. However, most isotopic composition of precipitation in humid regions corresponds to this relationship for most continental stations. The slope of isotopic composition of precipitation may vary from place to place base on the environmental parameters affecting the rain water prior to reaching the ground.

A local Meteoric water line (LMWL) was determined using the isotope data of the rain water from the study area. This plot would aid in the discussion of the origin of surface water and groundwater in the Gushiegu and surrounding areas. The rainwater slope line was defined by equation 4.4

$\delta D = 7.49\ \delta^{18}O + 5.5,\ r^2 = 0.89$ (4.3)

The regression equation obtained for groundwater and surface water (Evaporation line) samples were:

$\delta D = 6.88\ \delta^{18}O + 4.97,\ r^2 = 0.83$ (4.4)

and $\delta D = 5.64\ \delta^{18}O + 0.37,\ r^2 = 0.84$ respectively. (4.5)

When the isotope data from this study area were plotted, all the points for surface water were found below the GMWL and the LMWL which indicate evaporation (Fig. 4.6). There is a wide difference between the slope of the LMWL (7.49) and the evaporation line (5.64) defined by the surface water data. During evaporation, ^{16}O is fractionated into the vapor phase to a greater extent than ^{1}H, such that the residual water follows a slope on a δD vs. $\delta\ ^{18}O$ diagram that deviates from the GMWL. The greater the degree of evaporation, the further the water will plot off the Meteoric Water Line (MWL). Also the lower the relative humidity the greater the angle of deviation between the MWL and the evaporation line (Clark and Fritz, 1997; Seal, 2003).

The difference in slopes of the surface water (evaporated water) and the global meteoric water lines makes the identification of evaporated water possible base on δD and $\delta^{18}O$ values and its deviation from the local meteoric water line (LMWL). The point of intersection of the evaporated line and the local meteoric water line is an indication of the source and isotopic composition of the surface water before experiencing kinetic isotopic fractionation. The value obtained at the point of intersection for both δD and $\delta^{18}O$ are -15.5 ‰ and -2.81 ‰ respectively (Fig. 4.6). This value compared to the average isotopic signature of the surface water (3.95 for δD and 0.63 for $\delta^{18}O$) is highly depleted with respect to the heavy isotope which means the surface water has undergone kinetic fractionation due to evaporation and transpiration. These values also compared with the average isotopic composition of precipitation (-56.37 for δD and -8.27 for $\delta^{18}O$) showed a very wide range in their isotopic signature which might be as a result of mixing of different isotopic signatures. Thus the existing surface water is highly enriched in the heavy isotope due to high ambient temperature, mixing with the recent precipitation may lead to such an isotopic signature of surface water prior to evaporation.

These mixed signatures make the surface water prior to evaporation more enriched in the heavy isotope than the precipitation. Few groundwater samples were found on and around the point of intersection between the evaporation line and the local meteoric water line (LMWL) which is an indication that the aquifers at those sampling points were recharge from the surface water prior to evaporation. These might also happen because those wells (GH 05, GH 09, GH 33 and GH 40) were at shallow depth and were also located at very low land areas in the districts, since most of the surface waters were dams and rivers which are tributaries of some major rivers like Nasia.

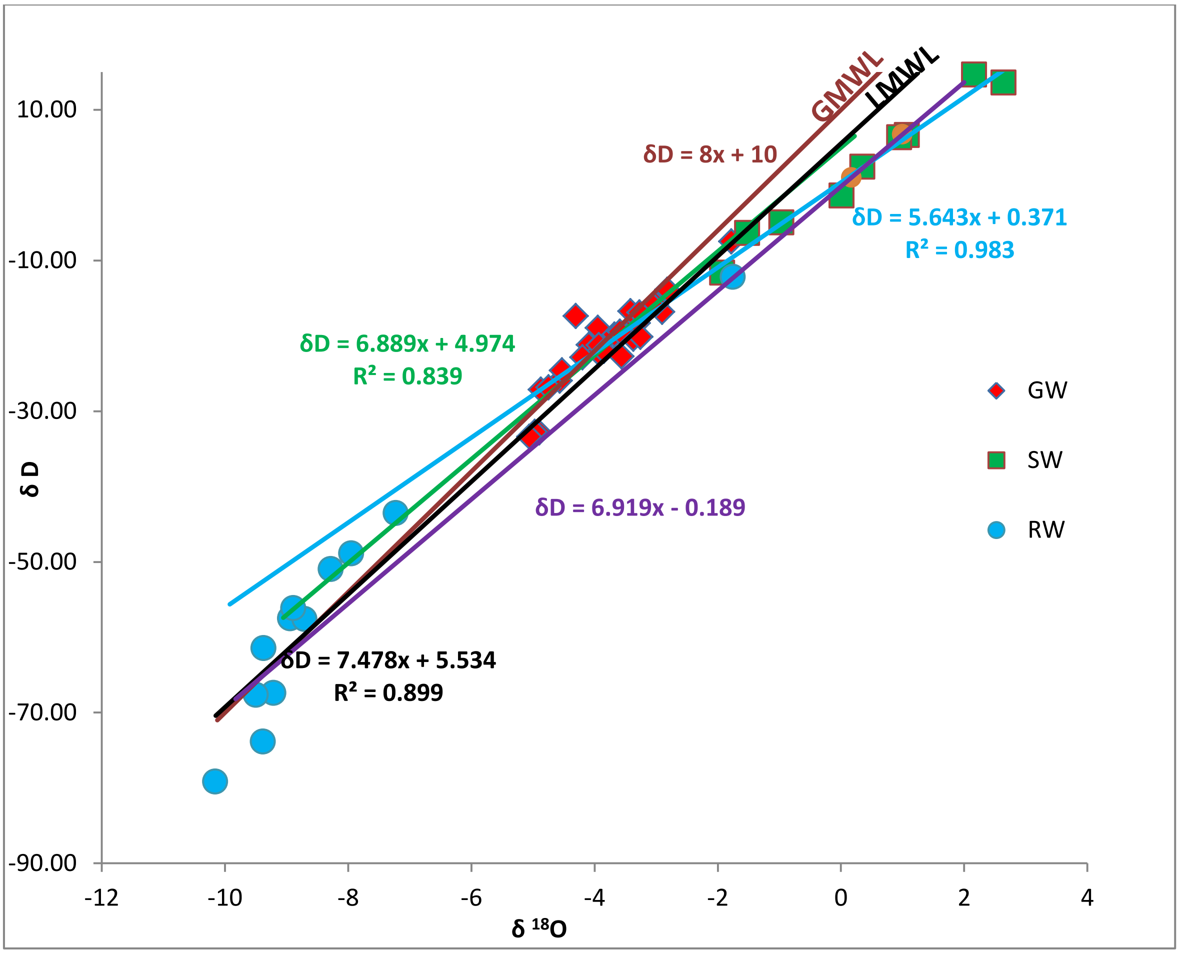


Figure 4.6: A graph of δD against δ^{18}O showing the relations of the isotopic compositions of groundwater, surface water and precipitation.

The LMWL (equation 4.3) has a lower slope and d-excess values compared with the GMWL suggesting evaporation of rain drops leading to slight enrichment relative to the GMWL. The lower slope may also indicate that the rain water may have been sampled at lower relative humidity less than 100 % (Yidana and Koffie, 2013). At lower relative humidity the lighter isotopes are evaporated back into the atmosphere leaving the residual rain water enriched in the heavy isotopes. Evaporation under a relative humidity of less than 100 % will result in a slope of 5±2 on a δD – δ^{18}O plot (Yidana and Koffie, 2013).

The line (violet) attributed to Pelig-Ba (2009) in Figure 4.6 is different from the local meteoric water line (LMWL) obtained from this study comparing their $\delta^{18}O$ coefficient (slope) and deuterium excess values. The d-excess value and $\delta^{18}O$ coefficient is humidity and air mass temperature dependent (Dansgaard, 1964: Merlivat and Jouzel, 1979) and this may explain why LMWL has a larger coefficient and d-excess value than Pelig-Ba line. Pelig-Ba (2009) obtained the rain samples from two different years 2007 to 2008 and the relative humidity at the time of sampling might differ. However, lighter rain in the Northern Region of Ghana may also lead to enrichment in the heavy isotopes since the region is located in the dry savannah climatic zone. Hence samples taken during the peak of the dry savanna climate (Northeast trade winds) could be more evaporated (Pelig-Ba, 2009). In addition, Pelig-Ba's samples were not localised in Gushiegu but in the whole Northern Region of Ghana and this may lead to the variation in the coefficient and d-excess value.

The LMWL of Akiti (1986) in the coastal environment of the Densu Basin in the southern Ghana compared with the LMWL of this study show quite similar slope (Equation 4.3 and 4.7). However the intercept of this study is lower than of Akiti (1986), which suggest relative enrichment of the rain water in the study area. The enrichment might be due to high ambient temperature in the study area which might have taken the lighter phase of the rain water leaving the residual phase enriched in the heavy isotopes. During the fall of water from the cloud to the ground the rain drops might have been subjected to evaporation and exchange with the environmental vapour. These processes are, thus, important for the final composition of liquid precipitation when it reaches the ground (Dansgaard, 1964). Furthermore, the observed trend in the slope and intercept of this study is reasonable compared to Akiti (1986) because rainwater samples were taken by Akiti about 26 years ago and since then Ghana as a whole has experienced a number of drought years as a result of climatic variability. These drought years is characterized by high temperature and low relative humidity leading to lower d-excess values and therefore making the rain water relatively enriched in the heavy isotopes.

$$\delta^{2}H = 6.9\delta^{18}O - 0.19, r^{2} = 0.91 \qquad (4.6)$$

$$\delta^{2}H = 7.86\ \delta^{18}O + 13.61 \qquad (4.7)$$

The trend of the slope (LMWL) and the intercept of this study is higher than obtained by Acheampong and Hess (2000) in the Southern Voltaian, with a slope of 7.02 and intercept value of 4.3 (equation 4.8). The relatively lower slope obtained by Acheampong and Hess (2000) could be attributed to difference in humidity and the amounts of rainfall. These samples were taken during or close to the end of the rainy season when the rainfall amount were lighter, and humidities were considerably less than 100% (Yidana and Koffie, 2013; Acheampong and Hess, 2000). Larson et al. (2000) also attributed smaller slopes of meteoric water lines to cycles of evaporation and condensation during atmospheric transport of water vapour from the oceans. Lighter rainfall experience much fractionation due to evaporation, since continental air masses may retard it speed before reaching the ground. The more time it spends in the atmosphere as a result of air mass movement the more fractionated it becomes leaving the residual rain more enriched in the heavy isotopes.

$$\delta D = 7.02\ \delta^{18}O + 4.3, r^{2} = 0.98 \qquad (4.8)$$

The plot of δD against $\delta^{18}O$ for precipitation (LMWL) with equation 4.3 from current study has shown similar trend in slope to that obtained by Yidana and Koffie (2013) (equation

4.9). However the intercept of the LMWL of this study is slightly lower than that obtained by Yidana and Koffie (2013), which suggest enrichment as a result of evaporation. Similar slopes were expected because the samples were taken at the same place thus Tamale but different times within the year. The rain samples in this study were sampled at the later end of the raining season where lighter rains are given off and might have suffered evaporation due to amount effect.

$$\delta D = 7.56\ \delta^{18}O + 6.67,\ r^2 = 0.904 \qquad (4.9)$$

4.1.2. Stable Isotopes in Surface Water in the Study Area

The surface waters (rivers, streams or dams) data for δD and δ^{18}O, respectively, fall in the ranges of -11.85‰ to 20.29‰ and -1.92‰ to 3.53‰, with average of 3.95‰ and 0.63‰. The variance of δD and δ^{18}O for the dataset, are respectively 105.3‰ and 3.25‰, suggesting significant variation in the dataset of each isotope. The high variances suggest significant difference in their isotopic composition, which also implies different rate of evaporation of the surface water in the study area. The isotopic compositions appear to be mainly affected by evaporation since most of the surface water bodies were exposed to sunlight. It might not be as a result of base flow because generally the study area is mainly low lands. The surface water samples lie on an evaporation line (equation 4.5) and intercept with the GMWL at -22.64 ‰ and -4.08 for δD and δ^{18} O respectively. The isotopic signature of these intercept represent the mean isotopic composition of the parent rainwater (Yidana and Koffie, 2013). The intercept between the LMWL and the evaporated line also reveals the isotopic composition of the surface water prior to evaporation as already established. These series of values of intersection between GMWL and evaporation line (-22.64 ‰ for δD and -4.08 ‰ for δ^{18}O) and LMWL and evaporation line (-15.5 ‰ for δD and -2.81 ‰ for δ^{18}O) compared with the mean isotopic composition of the surface water (3.95 ‰ for δD and 0.63 ‰ for $\delta^{18}O$) tells the stages of fractionation that took place. This tells the extent of enrichment the surface water (dams and ponds) which get it source from rainwater has undergone. This process of enrichment appears to be associated with fractionation as a result evapotraspiration.

GH04, GH08, GH15 and GH25 which were dams are highly enriched in the heavy isotopes of δD and δO^{18} compared to the other samples. This is obvious because the dams are stagnant and are exposed to the atmosphere for a long time and so heat and solar radiation subject these waters to fractionation processes due to evaporation effects as outlined previously. The rest of the samples indicated relatively less enriched isotopic composition because there was some vegetation cover of these waters which expose very little of the surface water to the sun's radiation.

The calculated deuterium excess of surface water ranges from 5.74 ‰ to 17.01 ‰ with an average of 9.2 ‰. As the $\delta^{18}O$ increases (more enriched) the deuterium excess in all the samples decreases gradually (Fig. 4.12). This observation can partly be attributed to dilution of the current surface water with different events of rainfall with different average isotopic composition with different degree of evaporation. Since some of the surface water are partly covered with vegetations.

4.1.3. Stable Isotopes in Groundwater in the Study Area

There were considerable variations in the isotopic content of the groundwater in the study area. The stable isotopic composition ranges from -33.38 ‰ to -7.49 ‰ and -5.05 ‰ to 1.78 ‰ for δD and δO^{18} respectively. From Figure 4.7, it is observed that most of these samples were plotted on or close to the GMWL which indicate that the groundwater is from meteoric origin. Generally, they are relatively depleted, considering the values of GH01 (-25.95 ‰ for δD and -4.56 ‰ for δO^{18}), GH06(-32.83 ‰ for δD and -4.89 δO^{18}), GH11(-27.15 ‰ for δD and -4.87 ‰ for δO^{18}), GH13 (-26.85 ‰ for δD and -4.75 ‰ for δO^{18}), GH20(-32.77 ‰ for δD and -4.97 ‰ for δO^{18}), GH22 (33.8 ‰ for δD and -5.06 ‰ for δO^{18}) compared with the surface water and very few were relatively enriched which might be due to evaporation. Some of the samples were plotted on or near the local meteoric water line (precipitation line) while others were relatively further away from the line (Fig. 4.7). The samples that were plotted close or on the line are likely to be recharged from the local precipitation.

Some of the samples were found above the LMWL, suggesting a recent recharge signature but they may have suffered some evaporative effect, which might result in fractionation hence enrichment of the groundwater. The clustering of the groundwater samples observed in Figure 4.7 suggests a well-mixed system with relatively constant isotopic composition. About 40 % of groundwater data plotted below the line (evaporation line) (Figure 4.6) is an indication of evaporative processes in the soil during infiltration (Kaka et al., 2011). The range of values for the isotope content for the groundwater reveal a narrow isotopic variation which suggest that all the groundwater samples might have originated from the same source of recharge or some water regime predominantly from rainfall (non-evaporated). The slight variation in their isotopic signature may also suggest that the waters have not mixed sufficiently to homogenize variations in the isotopic composition of recharge waters.

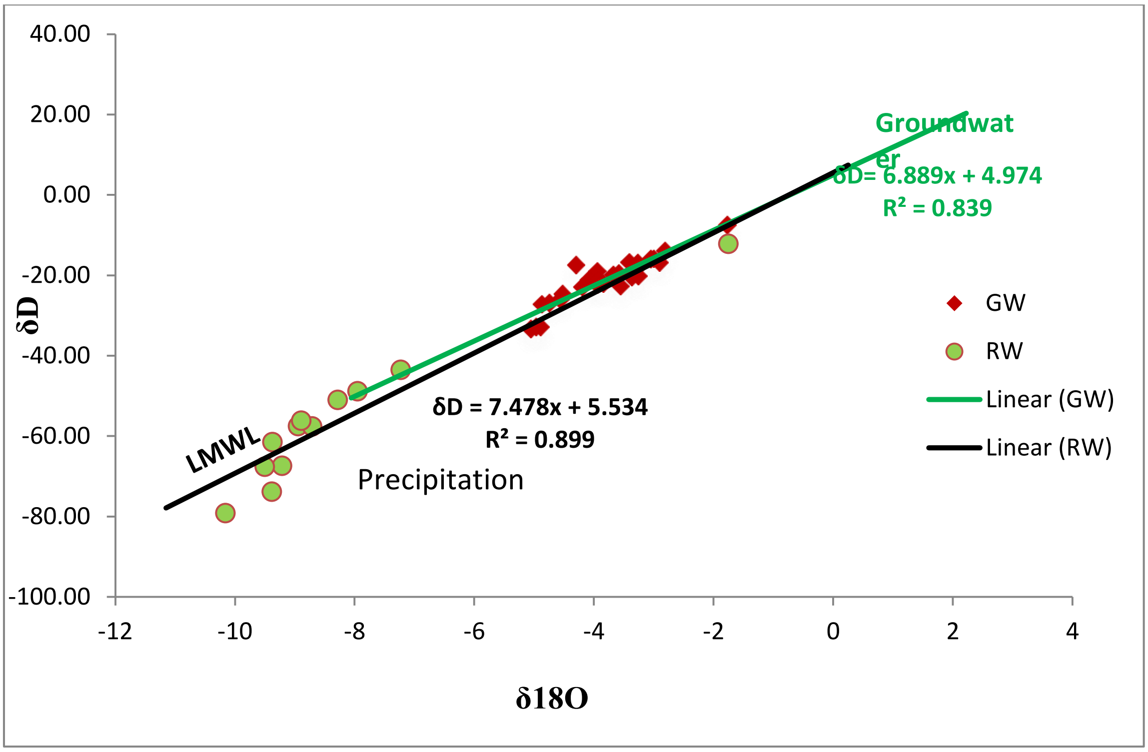


Figure 4.7. A graph of δD against δO^{18} for groundwater and rain water

The groundwater is comparatively enriched in the heavy isotopes (Fig. 4.3), because the Middle Voltaian from Pelig-Ba (2009) has a very low porosity due to high degree of consolidation and low fissuring. Which implies that rain water will not easily be percolated but be removed from the surface by evapotranspiration and fast runoff. The presence of hard and non-transmissible pan underneath the top soil also constitutes significantly to evapotranspiration and runoff. Furthermore, the enrichment of the groundwater may also be due to shallow depth aquifers in the study area which might allow easy heat flow into the water table during the hot days and dry seasons. A more depleted stable isotope of rain water recharging an aquifer can also alter the isotopic signature already existing.

Pelig-Ba (2009) ascertain that groundwater along the north-eastern margin of the Northern region of Ghana are more depleted than those in the south-west. Comparing the groundwater slope and intercept of this study to Pelig-Ba (2009), the current study has a higher slope 6.88 than the former 5.7 making it relatively depleted. Such observation was expected because the groundwater samples collected by Pelig-Ba (2000) were from two geological terrains with different environmental features, the Basement Complex and the Voltaian. The Basement complex was observed to be more enriched in the heavy isotope due to high vegetation cover. Here the vegetation cover will intercept the rain water and may cause it to fractionate, leaving the residual rain to be enriched in the heavy isotope prior to recharging. Transpiration as a process of removing the lighter isotope from groundwater in that geological terrain is more dominant compared to the current study which has relatively less vegetation cover making it more depleted. Current study groundwater plots also have a lower intercept 4.97 compared to 5.64 Pelig-Ba (2009). This observation may be influenced by local effect because of differential ambient temperature and relative humidity.

The point of intersection between the LMWL and the groundwater line (GWL) depicts the isotopic signature of precipitation that recharged the aquifer after fractionation and transpiration in the unsaturated zone. The determined value at this point of intersection for δD and $\delta^{18}O$ is -1.51 ‰ and -0.94 ‰ respectively. The isotopic composition at this point is somewhat higher than the intersection between LMWL and the evaporated line (EP) (-15.5 ‰ for δD and -2.81 ‰ for $\delta^{18}O$) which is the composition of the surface water prior to evaporation. Thus the intersection between LMWL and GWL isotopic signature are relatively enriched in the heavy isotopes compared with the intersection between LMWL and EP. This is so because the rainwater before getting to the water table might have undergone a lot fractionation due to evapotranspiration at the unsaturated zone and the root zone. Figure 4.7 also shows a very narrow variation between the slop of the groundwater isotopic plot and local meteoric line (precipitation), which also confirms that the groundwater might be from the meteoric regime.

4.2. Geochemical Evidence of Recharge

4.2.1. Evidence using δO^{18} Versus Depth

The relationship between δO^{18} and depth to water level in meters is shown in Figure 4.8. Generally the groundwater in the study area is at a shallow depth which range between 0.63 m to 8.82 m. There is not much variation in the isotopic component of the groundwater as the depth to water increases. This is an indication that the water might be from the same isotopic sources and that stable isotopic composition of the groundwater is not interrupted as a result of mixing between deep waters (paleo) depleted in heavy isotopes and shallow waters (recent) enriched in heavy isotope. The isotopic signature of the groundwater with depth is generally homogenous of δO^{18} values as shown in Figure 4.8. This can also confirm the fact that the groundwater is from meteoric origin and that it is recent.

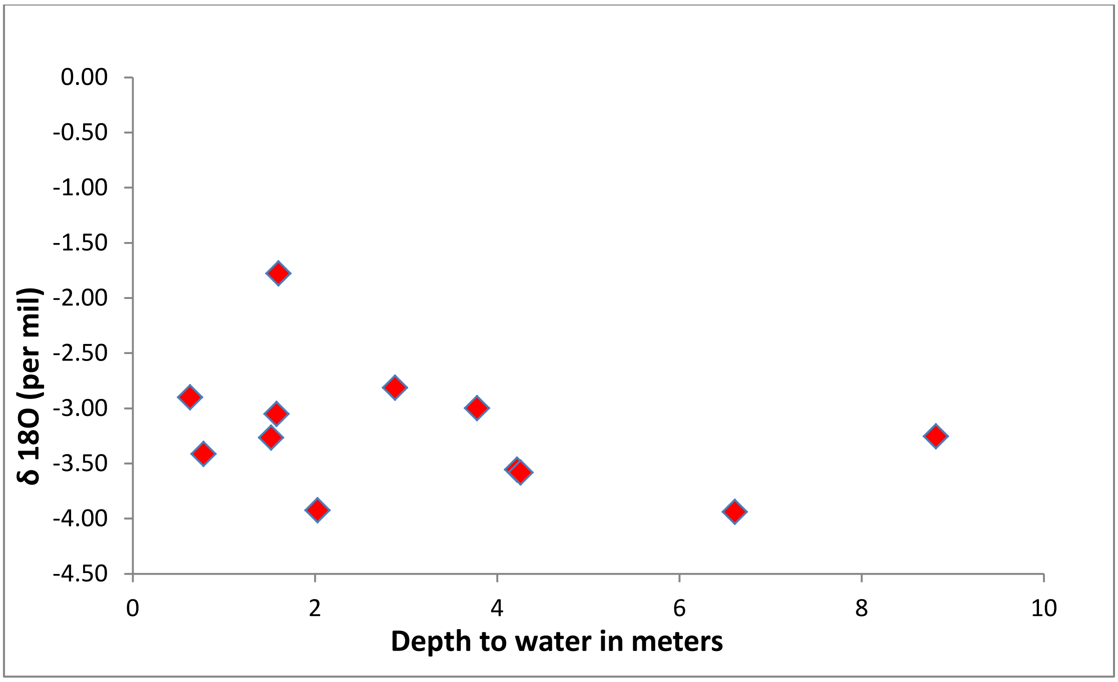


Figure 4.8. A graph of δO^{18} against depth to water showing the very slight variation of isotopic content with depth.

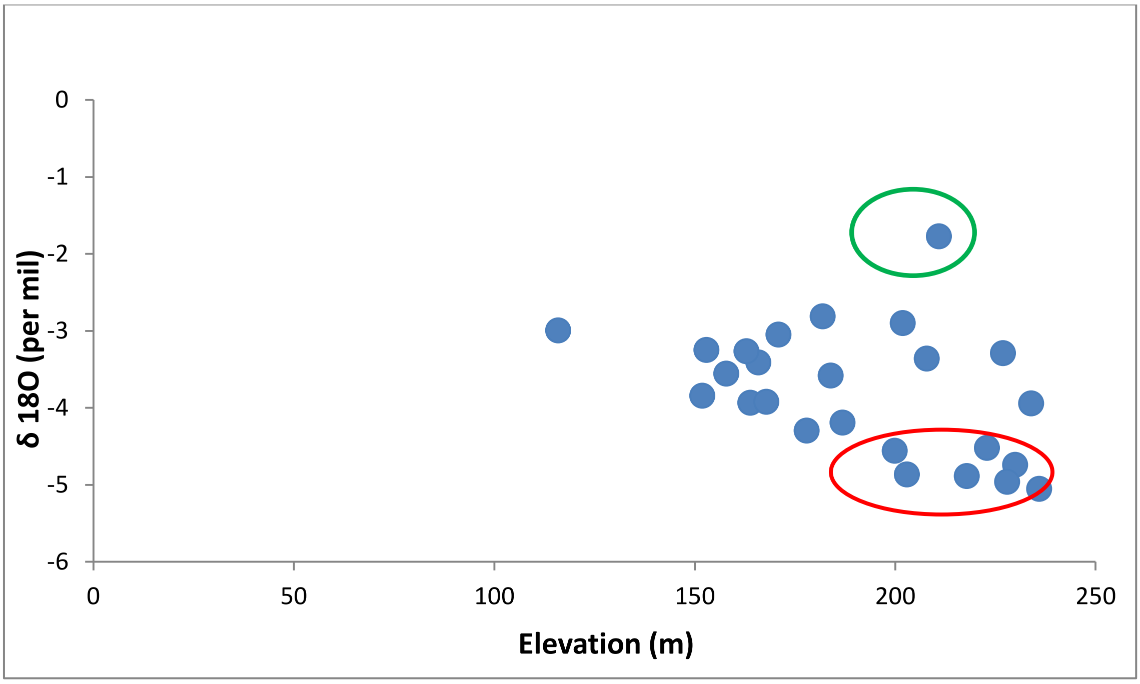


Figure 4.9. A graph of δO^{18} against elevation showing some variation in the isotopic signature.

4.2.2. Evidence Using Total Dissolve Solids versus δO^{18}

Electrical Conductivity and TDS (Salinity) increases simultaneously as the groundwater moves and interacts with minerals from the surface or bed rocks. The increase in total dissolved solids (TDS) values takes place without a significant change in isotopic composition, which may be due to mineralization (Fig. 4.10) (Gabrilla et al., 2010). As it has already been established that, the groundwater is from meteoric origin, it also means the groundwater in the study area is recently recharged. From Figures 4.9 and 4.10, thus the plot of δO^{18} against elevation reveals that samples at higher elevations are relatively depleted compared to samples at lower elevation. This might be as a result of long distance travel of precipitation prior to recharge of groundwater at lower elevation which might have been fractionated as it travels along it path, making it relatively enriched in the heavy isotopes. This cannot be generalised because there is not much variation in the elevation data in this study area, which is mainly low land area with some gentle slopes. Groundwater samples found at higher elevation (GH19; 228 m, GH 20; 236 m, GH 13; 230 m, and GH06; 218 m) showed a corresponding lower value of δO^{18} (depleted) as shown in red circle of Figure 4.9. Generally there is not much variation in the isotopic signature of the groundwater against elevation with the exception of the GH09, the "special well" (Fig. 3.3) which has caved in and exposed to the sun's radiation and however its isotopic signature enriched in the heavy isotopes.

If evaporation was the only process influencing the solute load of groundwater, $\delta^{18}O$ values would increase with increasing Cl concentration (Petrides et al., 2006). Groundwater with high Cl concentrations and low $\delta^{18}O$ values is an indication that transpiration played a major role in the fractionation (Petrides et al., 2006). High salinity of the groundwater requires a higher degree of concentration than what prevailed in this study, if salinity is as a result of water rock interaction (Petrides et al., 2006). This is suggesting that transpiration and evaporation are the more important processes controlling groundwater chemistry in the area since the TDS is relatively low compared with areas where the water chemistry is controlled by the geology. The low TDS values confirms that the water is meteoric in origin and had not had much stay in the aquifer system to have dissolved much solute into the groundwater system. It's also means that there is not much lateral flow in the aquifer systems.

δO^{18} - TDS relationship (Fig. 4.10) shows the groundwater follows a trend of salinity increase without a significant isotopic enrichment. It was also observed that some of samples with high TDS are relatively enriched in the heavy isotopes and these samples are found in lower elevation areas (Fig.4.10). Some of the samples at high elevated areas are also found to deplete in the lighter isotopes comparatively. Apparently, there has not been a precise trend in the scatter plot of each of the stable isotopes and groundwater TDS (or EC) in the study area. This observation buttresses the assertion that groundwater in the study area is of recent recharge, and most probably resulted from infiltrations of rainwater, a process whose rates are quite variable in space due to variable vertical hydraulic conductivity of the material vadose zone (Yidana and Koffie, 2013). Thus different activities in the study area might have influence the rate of recharge and also due to secondary porosity of the aquifer in the area it might lead to poor percolation, reducing the rate of recharge. The two “special wells” revealed a very low TDS values and were comparatively enriched in the heavy isotopes because they were at a shallower depth (Figure 4.10).

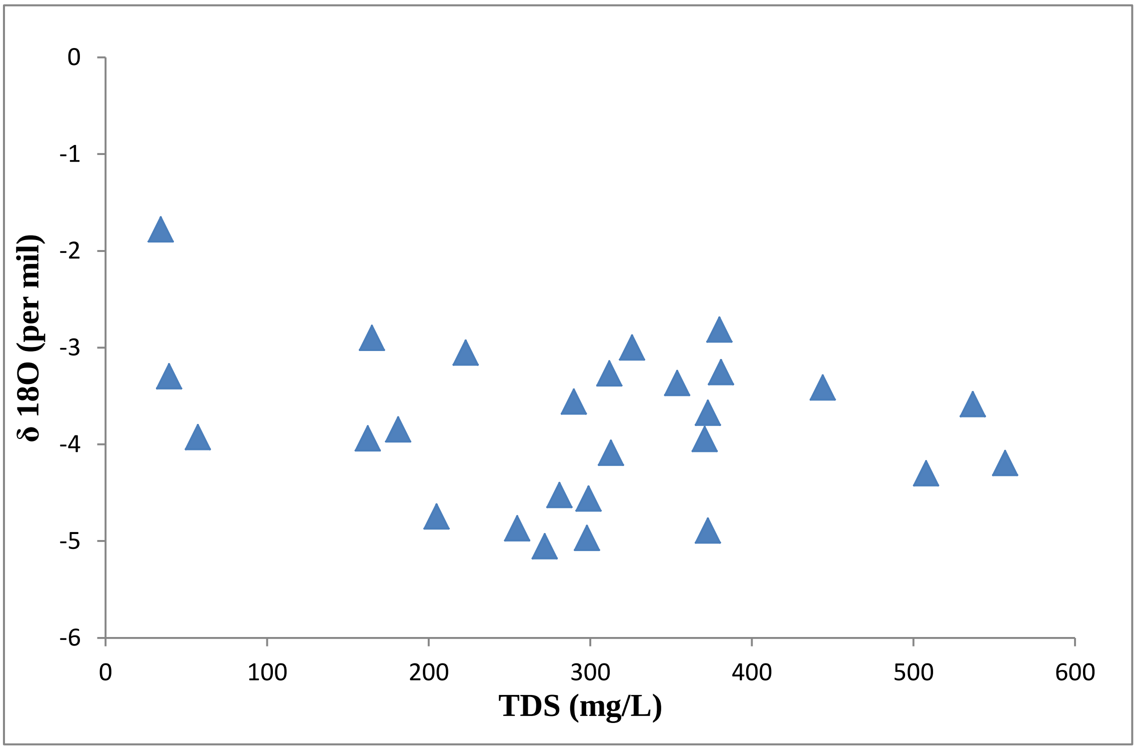


Figure 4.10. A graph of δO^{18} against TDS.

4.2.3 Mixing Processes

Mixing processes between groundwater and surface water are represented in Figure 4.11 showing the relationship between chloride and δO^{18} values. Most of the groundwater and surface water samples have low chloride values (< 50) which suggest that both waters have not dissolved enough soluble salts with the exception of GH40 which has extremely high values. The relatively low chloride values in groundwater may suggest fresh waters from precipitation. On the other hand high concentration of chloride in GH40 shows that

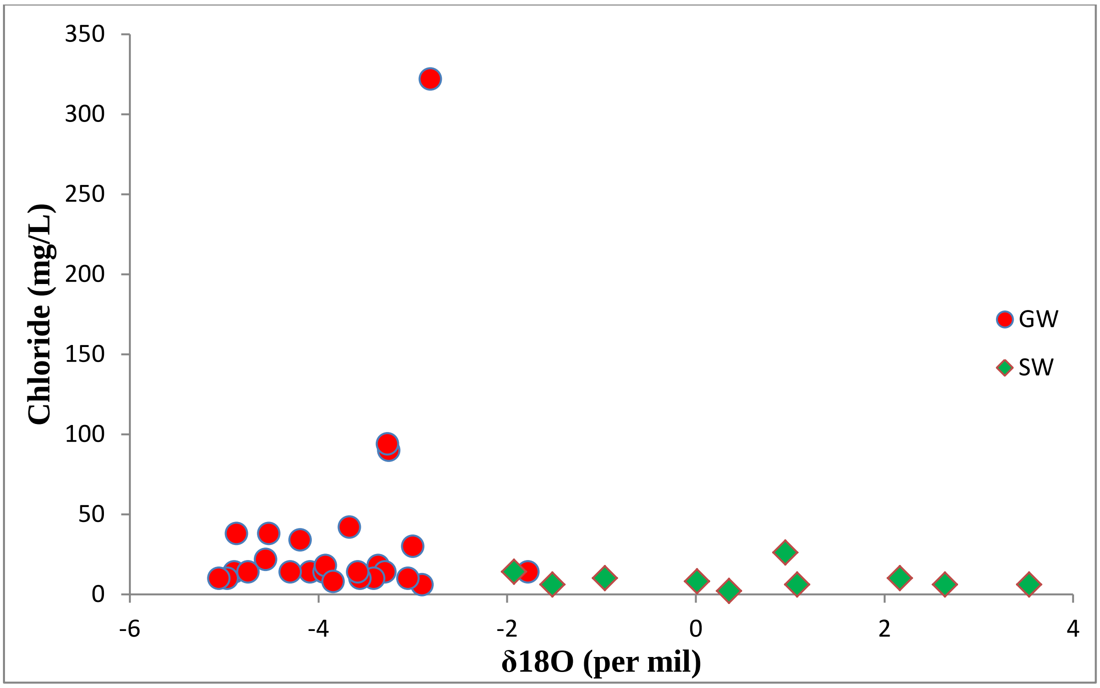


Figure 4.11. A relationship between chloride and oxygen – 18 (Groundwater - GW and Surface water - SW).

the sample might have undergone much dissolution hence the vast chloride variation relative to the other samples. It might also be attributed to anthropogenic activities because that well (GH40) was located in the Gushiegu Township where a lot of activity takes place. Figure 4.11 shows a large isotopic signature difference between the groundwater and surface water, which means there is little or no mixing between the groundwater and surface water. That is the surface water might not interact with the groundwater in any way that may lead to recharge. Figure 4.11 also shows uneven variation of surface water isotopic signatures leading to heterogeneity of it composition. This depicts that the individual surface water outlet is affected by the prevailing environmental conditions. This is true because some of the surface water in the study area (especially small ponds and dams) were partially covered by shade from plants grown along the ponds, dams and stream. Others have a broad surface area exposed to the sun radiation and therefore will be more fractionated and hence relatively enriched in the heavy isotopes.

4.2.4 Evolution of the Stable Isotope Composition of the Rain Water.

The deuterium excess (d-excess) reflects the conditions that lead to kinetic isotope fractionation between water and vapour during primary evaporation in the oceans (Dansgaard, 1964). This number also shows the extent of deviation of a given sample from the meteoric water line.

The d-excess value of the rain water (precipitation) ranges from 1.21 ‰ to 15.26 ‰ with an average of 12.7 and standard deviation of 1.62 (Fig. 4.5). The plot of d-excess against δO^{18} showed much variation in the d-excess values and slight variation in δO^{18} values with the exception of TM 12, which presupposes that the precipitation took place under different weather conditions since the samples were taken at different times in the year (Fig. 4.12). Isotopic composition of rain water is as a result of interactions between humid marine air masses and dry continental air masses (Gat and Carmi, 1970).

Figure 4.6 reveals a slight difference in slope between the LMWL (precipitation) and the GMWL of 7.49 and 8.0 respectively. This is expected because generally the Northern Region of Ghana is noted for its high environmental temperature and dryness and during rain fall, rain drop from the cloud to the ground might have been subjected to evaporation and exchange with the environmental vapour, hence influencing the final composition of liquid precipitation before it reaches the ground. Very low humidity in the area may also be a factor as described by Merlivat and Jouzel (1979). That could really be a factor because rain water samples were taken during or close to the end of the rainy season when the rainfall amount were lighter, and humidity were considerably less than 100%. Risi et al. (2008) also confirmed that rain water becomes relatively enriched as they re-evaporate.

The wider range of d-excess values of rainwater suggests different moisture sources of rainfall unlike Gibrilla et al. (2010). It further means that the rain water samples were not taken under a homogenized condition at the sampling points but in one way or other has individually been influenced by the environmental conditions prevailing at the time of sampling. The major process that may produce any significant difference in the stable isotopic composition of the rainwater is therefore the amount and intensity of the rainfall (Acheampong and Hess, 2000). Generally the d-excess values of the rainwater were influenced by the relative humidity and temperature of the area where the moisture originated (Merlivat and Jouzel, 1979).

The groundwater d-excess values ranges from 5.74 ‰ to 17.01 ‰, while those of the surface water range between -7.98 ‰ to 5.77 ‰ (Fig. 4.12). It can be observed that as the δO^{18} increases (more enriched) the d-excess in groundwater and surface water generally decrease gradually. It is also noticed that the groundwater d-excess values compared to rainwater d-excess values show similar range of values which presuppose that the groundwater is recharged from current precipitation but might have suffered some fractionation due to evapotranspiration.

Considering the δO^{18} values from Figure 4.12, the groundwater appears to be sandwiched between the δO^{18} values of the rainwater and surface water. This observation can be partly attributed to the dilution of the groundwater with the rainwater which could increase the d-excess (Yuan and Miyamoto, 2008). The gradual decreasing in the deuterium excess of collected groundwater samples with increasing δO^{18} indicates that, the current groundwater mixes with different rainfall events with different average isotopic values undergoing different degree of evaporation before recharge (Gabrilla et al., 2010).

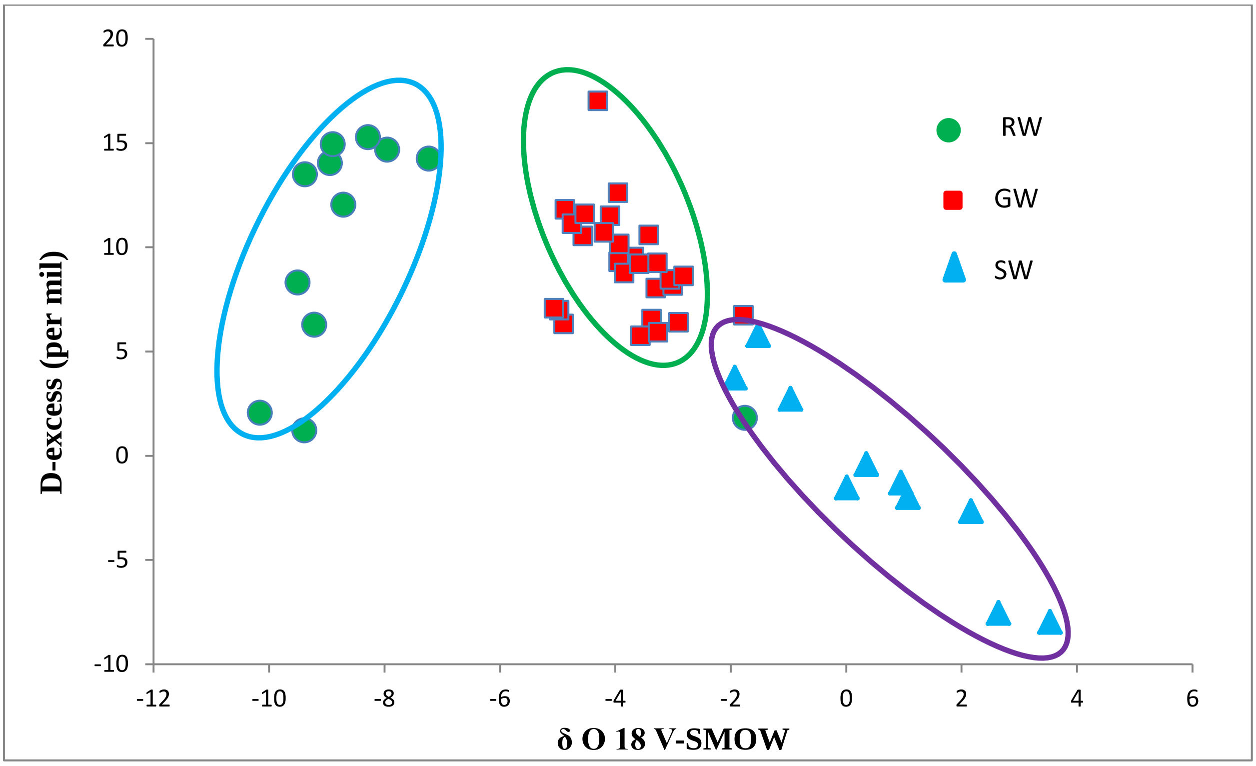


Figure 4.12. A relation between D-excess and δ ^{18}O showing some variations (Groundwater-GW, Surface water-SW and Rainwater-RW).

4.3 Estimation of Evapotranspiration and Groundwater Recharge

Quantification of groundwater recharge and its spatial trends are very important in groundwater resource management plans. It also serves as the bases to develop a good numerical groundwater flow model which can depict the real state (physical system) of the study area as much as possible. Concentration factor followed by the CMB methods were used to quantify the groundwater recharge and surfer 9 was also used to deduce the spatial variation of the recharge.

Concentration factor was used to determine how much of precipitation has actually been evaporated. The chloride concentration of the rain water ranges from 0.2 mg/L to 2 mg/L with an average of 1.31 mg/L and standard deviation of 0.16 mg/L. Generally the groundwater chloride concentration also ranges from 6 mg/L to 322 mg/L with an average of 33.63 mg/L and standard deviation of 60.6 mg/L. The concentration factor which is the ratio of chloride concentration of rain water to chloride concentration in groundwater was calculated using equation 3.1 and it ranges from 0.004 to 0.218 resulting in a percentage of 0.4 % to 21.8 %, with a mean of 0.089 (8.9 %) and standard deviation of 0.055 (5.5 %). Ritort (2007) outlined that a concentration factor of 0.25 indicates that evaporation process has caused a 4 times increase in the chloride concentration and thus 0.75 of the rain water might have been evapotranspired. Based on this it can be infered from the average concentration factor of 0.089 (8.9 %) that evapotranspiration has caused more than 11 times increase in the chloride concentration in the groundwater and therefore has led to about 0.911 (91.1 %) of the rain water been evaporated.

The average annual rainfall in the Northern Region of Ghana is estimated to be 1000 mm/yr (Anim-Gyampo et al., 2012; Attandoh et al., 2012; Yidana et al., 2012; Pelig-Ba,

2000). Appendix IV and Figure 4.13 shows the distribution of recharge rates base on Chloride mass-balance (CMB) equation by Allison and Hughes (1978) (equation 2.1).
For a good estimation of groundwater recharge using CMB method, it was assumed that there is no other source of chloride in groundwater beside precipitation. Even though weathering products from minerals and reworked sediments, can make a significant contribution of chloride concentration in groundwater it was neglected in this study. Because the boreholes and other groundwater outlets sampled were completed in sandstones and the weathered zone, where chloride has not been known to be a major mineral (Yidana and Koffie, 2013). Furthermore chloride concentration as a result of sea-water intrusion is also neglected because the study area is far from the ocean.

The assumption that precipitation is the sole source of recharge is not a challenge, provided the method is restricted to non-irrigated areas (Fouty, 1989). It was observed from the study area and with reference to Yidana and Koffie (2013) who worked in similar terrain that the use of chemical fertilizer and other agricultural chemicals on farms is very much on the lower side. And for that reason the contribution of chloride concentration from these sources may not have any significant influence on the groundwater. However, the assumption that all precipitation contribute to recharge can be a challenge, depending on the geological characteristics of the study area. But to overcome this challenge in unconsolidated sediments; the mean annual precipitation values should be used, because it most closely estimate potential recharge, even though infiltration may vary depending on soil porosity and permeability and topography (Fouty, 1989).

Inferring from the EC (68.4 – 1114 µS/cm) values of the groundwater; it suggest that the groundwater is relatively fresh, indicating that it is quite recent (Yidana and Koffie 2013;

Edmunds et al., 2006). These values also suggest that the groundwater had not remained in the aquifer system for too long and so had not dissolved much solute to have increased the chloride composition of the ground water. Furthermore the study area is not noted for any significant industrial activity that might affect the chloride increase in groundwater in the study; therefore the assumption that precipitation is the major source of chloride is justified.

The average groundwater recharge in the Gushiegu District based on the assumptions made earlier is estimated using CMB method to be 89.9 mm/yr and ranges from 13.9 mm/y to 218 mm/yr with the exception of Gh 40 which revealed a very low rate of recharge of 4.1 mm/yr.

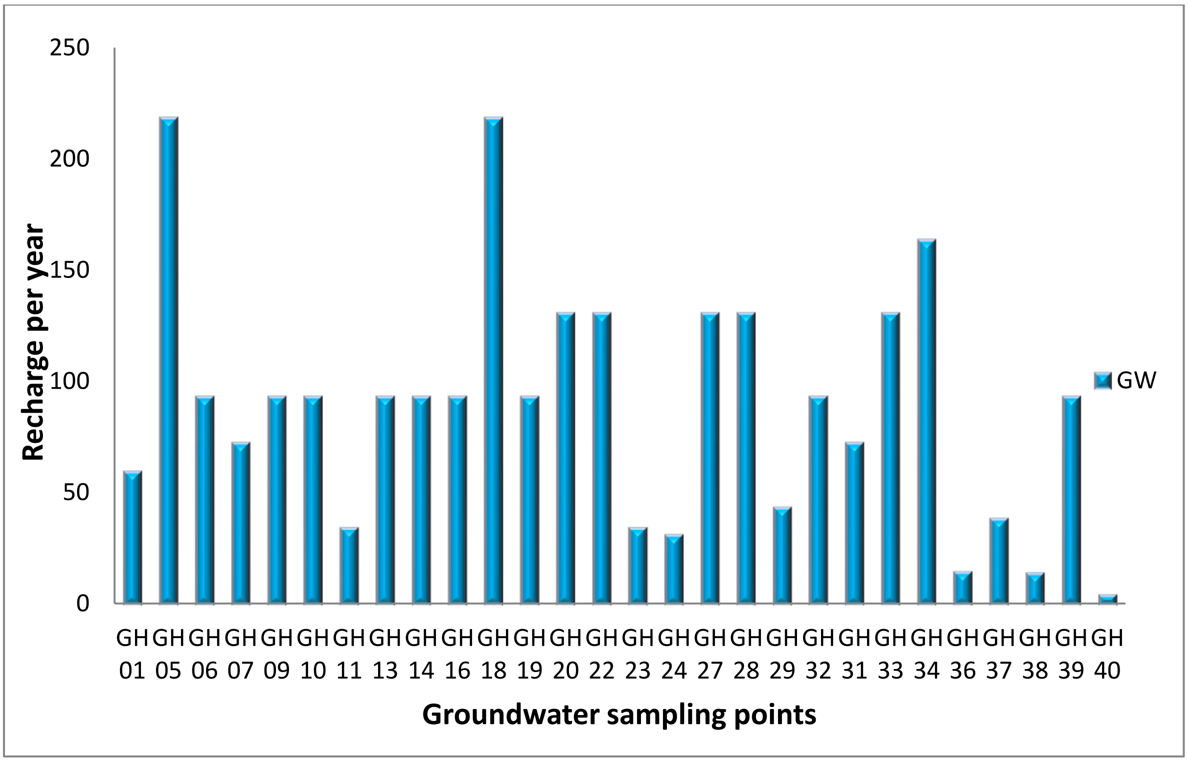


Figure 4.13. Bar chart showing the recharge rate at each groundwater sampling points.

This well had a very high elevated chloride which might be due to an anthropogenic activity, because the well was situated in the Gushiegu Township where a lot of activities take place.

It also reveals that about 911 mm/yr of the annual rainfall is lost through evapotranspiration and runoff. This value confirms the values obtained by the Water Resource Commission of Ghana in the White Volta Basin (IWRMP, 2008). They estimated that the evapotranspiration is 913 mm/yr, 910 mm/yr and 908 mm/yr in Tamale, Yendi and Bole respectively all in the Nothern Region of Ghana. Most of the precipitated water is lost due to evapotranspiration because the study area is underlain by rocks of the Middle Voltaian which comprises the Oti and Obosum beds, which are well consolidated and generally flat lying and therefore might reduce the rate of percolation. The beds are made up interbedded mudstones/siltstones, arkose and conglomerates (Dapaah-Siakwan and Gyau-Boakye, 2000). Dickson and Benneh (1995) also confirmed that heavy rains experienced during rainy season are often lost as runoff and evapotranspiration with minimal recharge to aquifer.

The wide variation in the chloride concentration of the groundwater which has led to a wide variation in groundwater recharge rate in the study area (Figs. 4.13, 4.14 and 4.15) may be attributed to the differences in the local vegetation near the respective well location, which directly affects the amounts of evapotranspiration that would occur. It may also be as a result of the thickness of the vadose zone and thus the amount of water that can evapotranspire from the top of water table. Most of the high recharged points are found to be open wells which are recharged directly from rainfall without going through much fractionation as a result of evapotranspiration (Fig. 4.14). As a result, the chloride concentration in those wells are very low and based on CMB method it can be deduced that the lower the chloride concentration in groundwater the higher the recharge and vice versa. Most of the open well isotopic compositions which have a higher recharge values were found to be closer to the isotopic composition at the point of intercession between the evaporated line and LMWL. The value obtained at the intersection for both δD and $\delta^{18}O$ are -15.5 ‰ and -2.81 ‰ respectively (Fig. 4.6) compared with the isotopic signature of highly recharged sample GH05 and GH18 (-16.82 ‰ for δD and -2.90 ‰ for $\delta^{18}O$ and -13.43 ‰ for δD and -2.39 for δO^{18} respectively) as shown in Appendix VI. The isotopic composition at this point of intersection is an indication of the source and isotopic composition of the surface water before experiencing kinetic isotopic fractionation. It further suggests that the open wells with higher recharge rates took it source from the surface water prior to fractionation in the form of direct run off into the open wells. Yidana and Koffie, (2013) confirmed that generally the ionic contents of open wells are noted to be lower, due to the dilution effects of rainwater.

It was also noted from the recharge map and the wireframe (Fig. 4.14 and 4.15) that there are very few highly recharged areas and as such those areas must be noted and protected for good groundwater management plan. Gushiegu District by observation is noted of open dams which store rain water for use during the dry season and most of these waters are lost due to intense sun radiation during the dry seasons. To reduce the large amount of this water loss it is advisable the communities build more open wells to store rain water and to aid in recharging the aquifer systems, since most of the open wells receive direct recharge and are least fractionated. Generally the rate of groundwater recharge in the study area is very low due to shallow aquifers and slow rate of percolation. The geological formations are inherently impermeable and this can be attributed to compaction and metamorphism of the rocks (Junner and Hirst, 1946; Dapaah-Siakwan and Gyau-Boakye, 2000). The hydrogeological conditions in the area are generally controlled by the secondary permeability in the form of fractures, fissures and crevice. Erde`lyi (1964) found that the Voltaian formation (supposed to be Middles Devonian) for most part consists of clayey sediments even the best of the sandstones are unsuitable for storing groundwater. These properties of the aquifer make the recharging water vulnerable to fractionation by evaporation. Thus before the percolation water gets to the saturated zone much of the percolation water might have been lost due to intense sun radiation thereby reducing the amount of water that get to the water table.

Inverse Distance Weighting (IDW) was used to predict the spatial variation of the estimated groundwater recharge and their isotopic composition of the study area using Surfer 9. The highly recharge areas are located in the southwest and the northeast of the study area while the central points and some parts of the northeast recorded low recharge. Figures 4.14 and 4.15 represent the maps showing the spatial variation of the groundwater recharge in the study area using the CMB. The recharge distribution in the area is uneven and unpredictable in the sense that it does not really show a distinct spatial pattern.

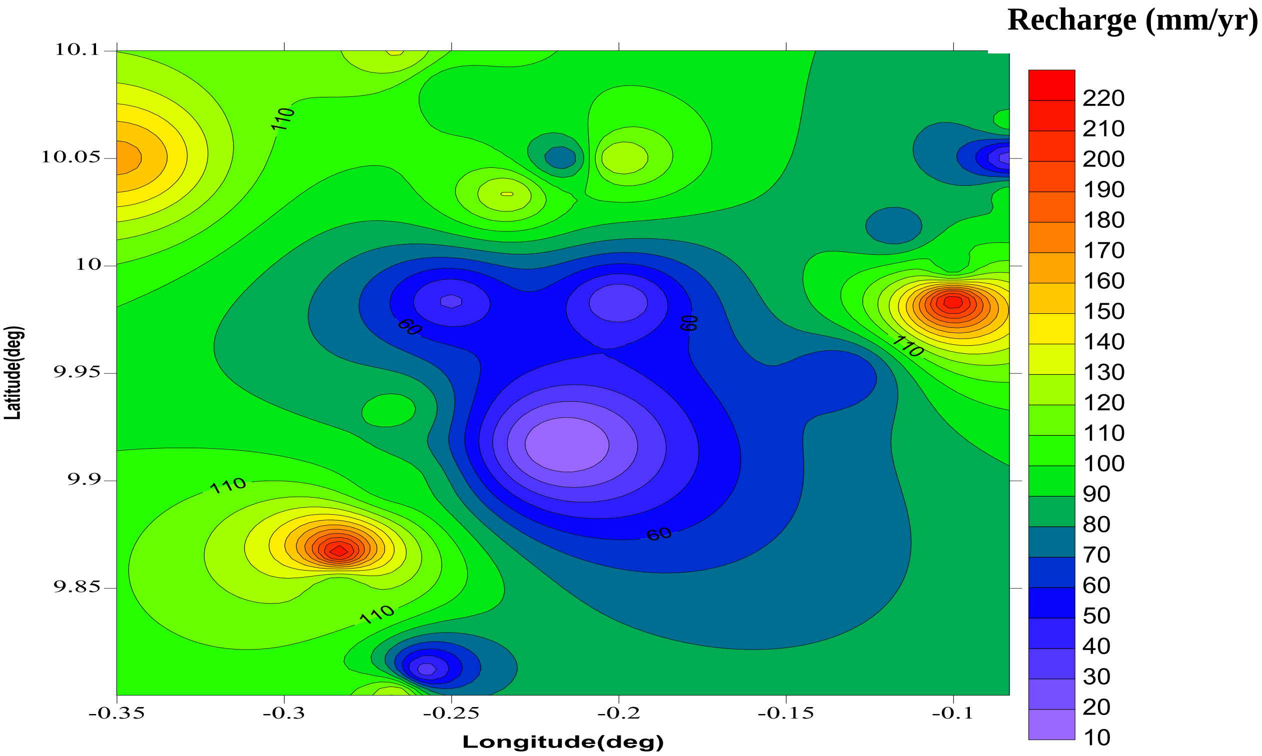


Figure 4.14. Predicted map of the estimated groundwater recharge in the study area.

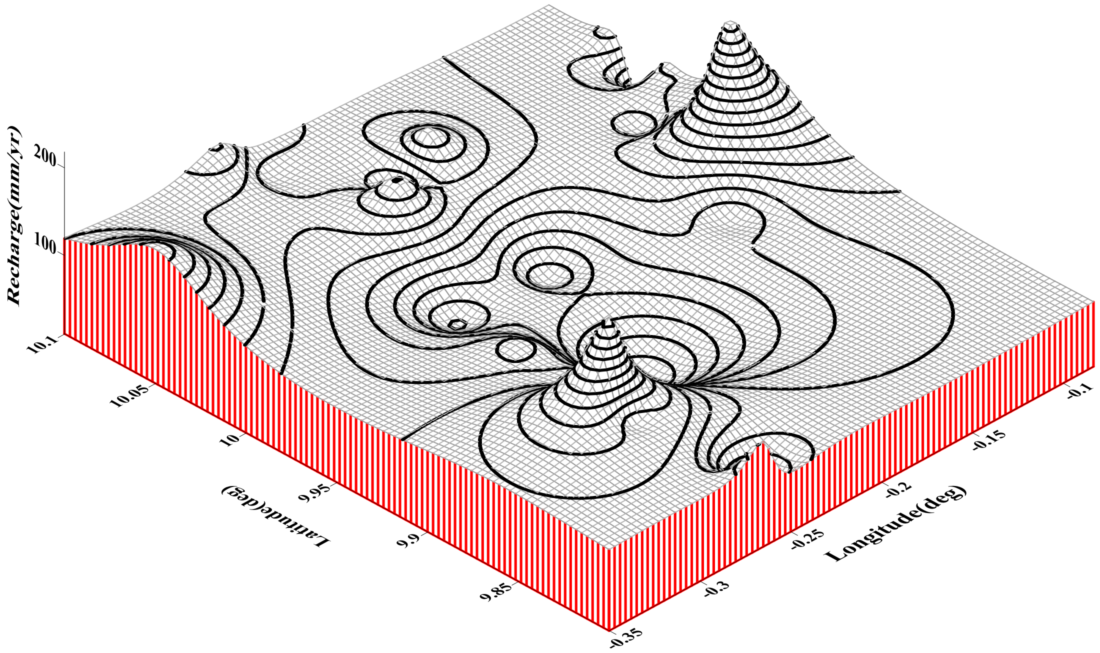
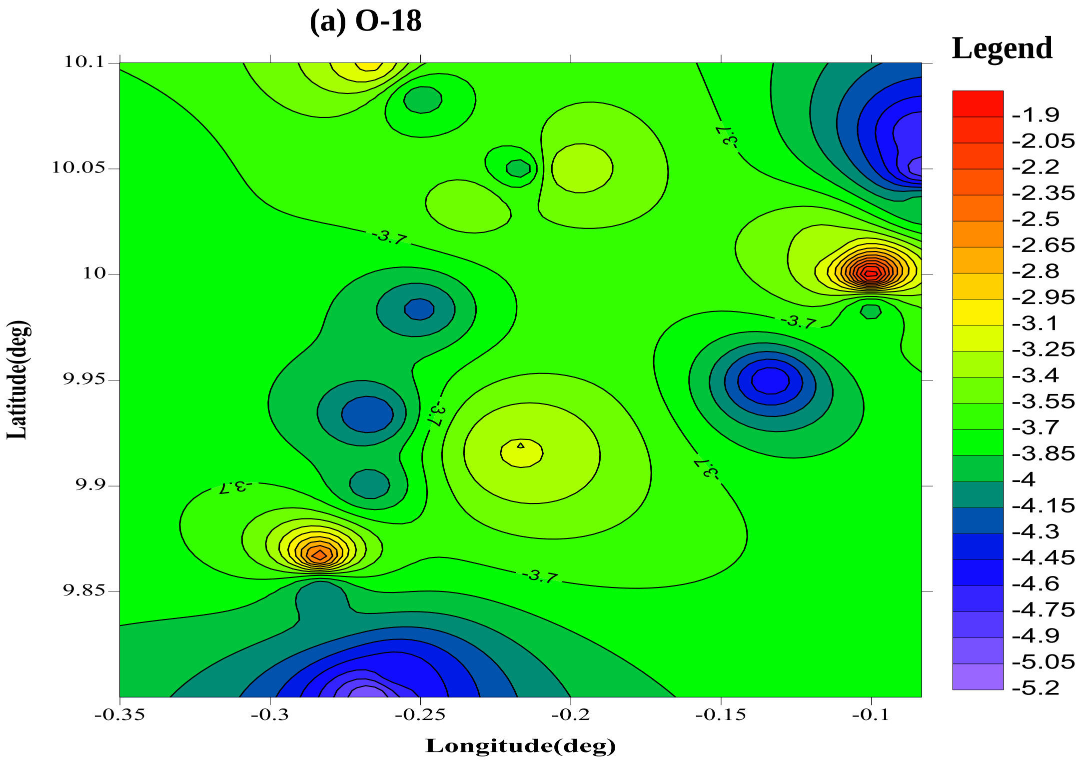


Figure 4.15. Predicted wireframe map of the estimated groundwater recharge in the study area.

In Figures 4.14 and 4.17, comparing the recharge rate distribution and both isotope distribution in the study area it was observed that the higher recharge areas in the southwest and some part of northeast were depleted in the heavy isotopes relative to the others, even though some of these areas were also relatively enriched. This confirms that generally the locations where groundwater recharge is relatively low, the heavier isotopes are quite enriched due to low infiltration and percolation rates, and the concomitant evaporative enrichment of the heavier isotopes (Yidana and Koffie, 2013). The highly recharged northeastern area of the predicted recharged map (Fig. 4.14) was found to be enriched in the heavy isotopes as compared with the predicted maps of the isotopes (Fig. 4.17), thus chloride was not conservative. It suggests that other processes other than evapotranspiration are influencing the chloride concentration of the aquifer in the area.



(b) Deuterium

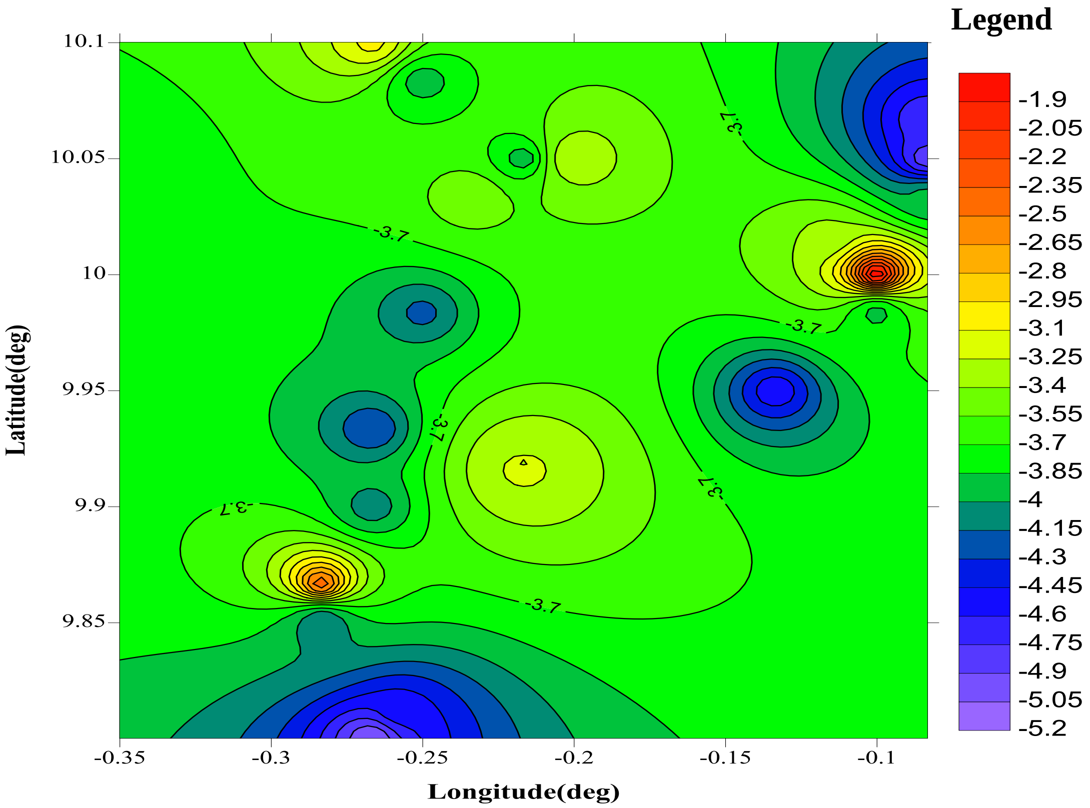


Figure 4.17. Prediction maps of the stable isotopes of δ^{18} O (a) and δD (b) in the study area

4.4 Estimation of Recharge Using Groundwater Level Data

Recharge based on the WTF method for unconfined aquifers in this study was calculated using Equation 3.3. The method is best applied over short time periods (hours or a few days) in regions having shallow water tables that show sharp rises and declines (Scanlon et al., 2002). This method is based on the assumption that groundwater recharge mostly occurs by vertical percolation and delayed drainage (Lee, 2005). This assumption is justified because there is no major river or stream in the area that might have partially recharged the aquifer due to base flow. Also based on my observation of the area it is not noted for sophisticated irrigation installations that might affect the recharge of the groundwater thereby increasing the water levels in the wells.

Groundwater recharge for each of the observed wells was calculated by multiplying the water level rise with the specific yield values of the aquifer material in which the wells are situated. The water level rise (Δh) in the observed wells was estimated using the recorded water level data. The water level rise is generally computed as the difference between the peak of a water level rise and the value of the extrapolated antecedent recession curve at the time of the peak (Delin et al., 2007).

The specific yield for the area was obtained from literature based on the aquifer material, which is made up of mudstone and shales (clay, sandy, loam). As established earlier, the aquifer in the area has low permeability and the porosity which is as a result of secondary event which took place after the primary porosity has been destroyed through compaction and slight metamorphism (Junner and Hirst, 1946; Bannerman, 1975). In view of this the specific yield of the area is estimated to be in the range of 0.01 to 0.05 since the area is in the fractured zone and in fracture-rock systems, the permeability of the matrix is usually very low, so the time required for it to drain is very long (Healy and Cook, 2002). These range of values were also considered based on the values used in India and the range of specific yield value (0.01- 0.05) were reported in Shahin (2002). It is generally assumed that specific yield varies with depth; especially in hard-rock aquifers where fracture density and porosity change with depth, namely between the different layers constituting the aquifer (Mare´chal et al., 2004). But in this study it was observed that most of the wells are shallow wells with an average depth to water of 3.25 m based on the available data and so specific yield might not vary that much with depth.

The calculated mean recharge of well WVB 12 for the year 2006, 2007, 2008, 2009 and 2010 were 39.4 mm/yr, 57.1 mm/yr, 114 mm/yr, 105 mm/yr and 42 mm/yr (Appendix

VIII) respectively and the cumulative average was 7.14 mm/yr. Well WVB 13 at Galwei also recorded an average 42.2 mm/yr and 120 mm/yr in the year 2006 and 2008 respectively with a cumulative average of 8.1 mm/yr. The cumulative average of the two well WVB12 and WV13 in the study area represent 7.14% and 8.1% of the annual rainfall. It also suggests that more than 90% of the annual rainfall is lost by other processes other than percolating to increase the water level in the aquifer. Evapotranspiration takes away a large amount of the rainfall before it gets to the water table. Similar method was used to obtain groundwater recharge at Korea with an estimated average recharge ratio of 12.7% for the whole basin area (867 km^2) (Korea Water Resources Corperation (KOWACO) (Lee et al, 2005). Lee et al., (2005), also obtained a recharge ratio based on cumulative recharge range of 2.5% to 20.1%. The estimated recharge value in the current study is very realistic because is within this range, which are of similar geological characteristics.

The difference in the recharge values for the five study years in well WVB 12 and two study years in well WVB 13 could be attributed to differences in the annual rainfall distribution and intensity. The hydrographs obtained (Fig. 4.19 - 4.25) from this study showed some variation in the water levels rise from year to year. This is so because of the variation in annual rainfall distribution and intensity of the rainfall in the study area. Although the rainfall season in the study area starts in April/May, water level in all wells started to rise in June/July when about 40 % of the annual rainfall had occurred with the exception of Figure 4.21. This observation may suggest that there is a lag of a month or two before recharge takes full effect. The lags suggest that there is non-linear relationship between rainfall and recharge in the study area. Additionally, the lag suggests that most wells in the study area recharge slowly.

Totin et al. (2008) also stated in his paper that large recharge of groundwater is observed during a long rainy season where cumulative rainfall caused rise of water table and water storage between April to October. Any noticeable water-level rise in case of no rainfall indicated existence of delayed drainage by preceding rainfall or horizontal component of groundwater recharge (Lee et al., 2005). It is not so surprising because due to low permeability as a result of secondary porosity it is expected that percolation in the study area be slow. Some of the years had shown some sort of relative fast recharge rate, thus within the said rainfall seasons which suggest very high intensity of rainfall during those years and due to shallow aquifer (Fig. 4.19, 4.20, 4.22, 4.23).

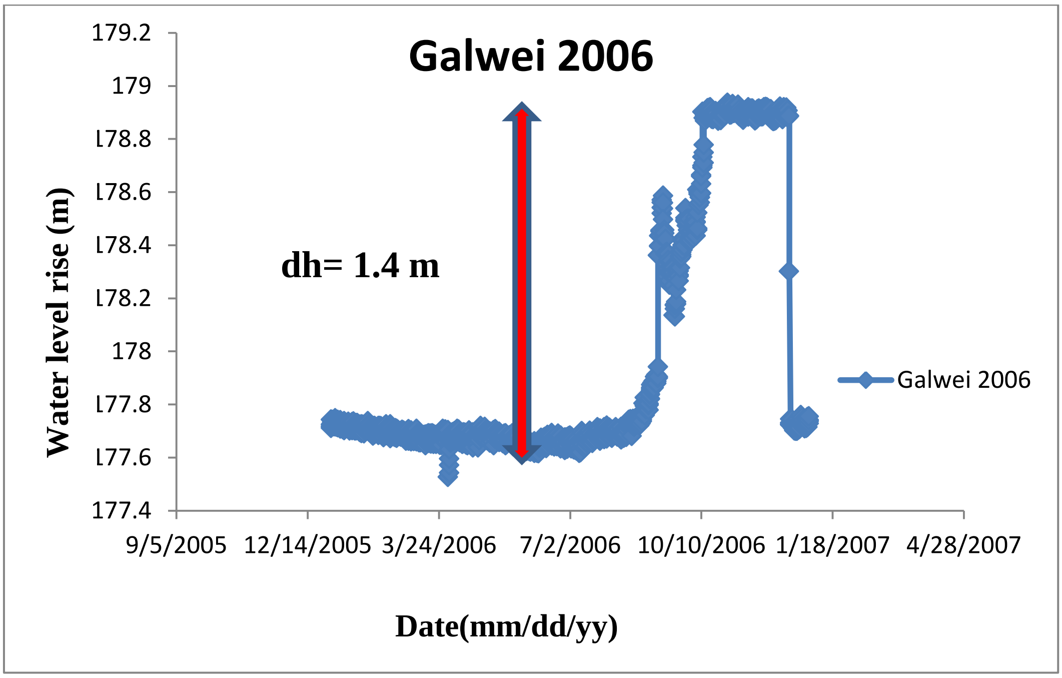


Figure 4.19. Groundwater hydrograph of well WVB13 in 2006

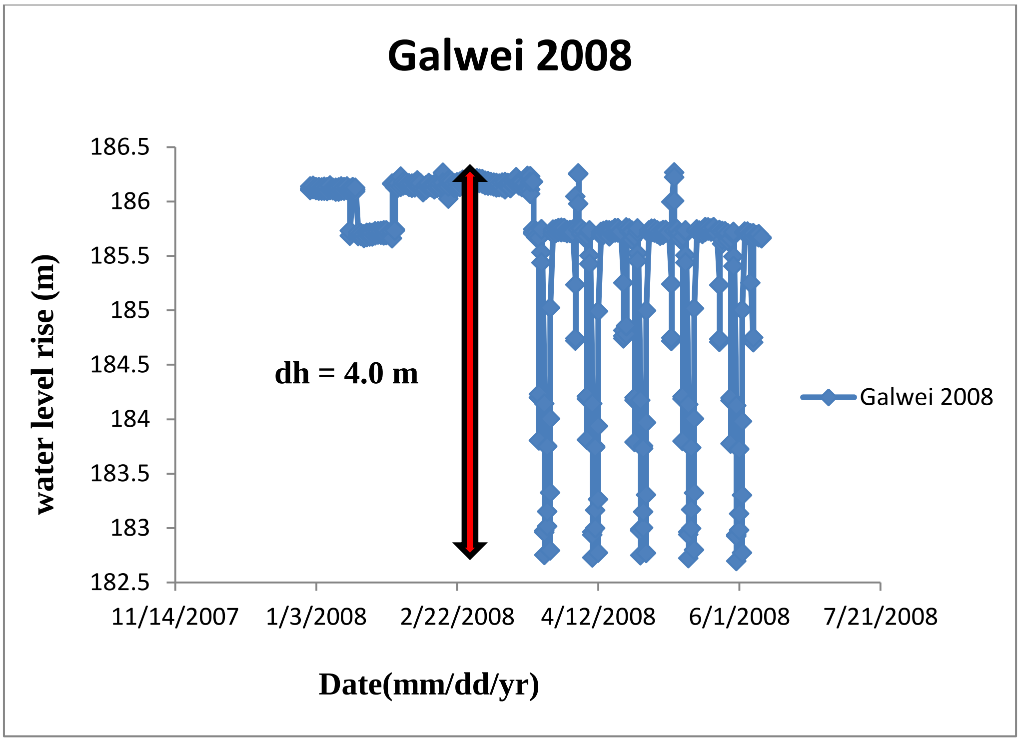


Figure 4.20. Groundwater hydrograph of well WVB13 in 2008

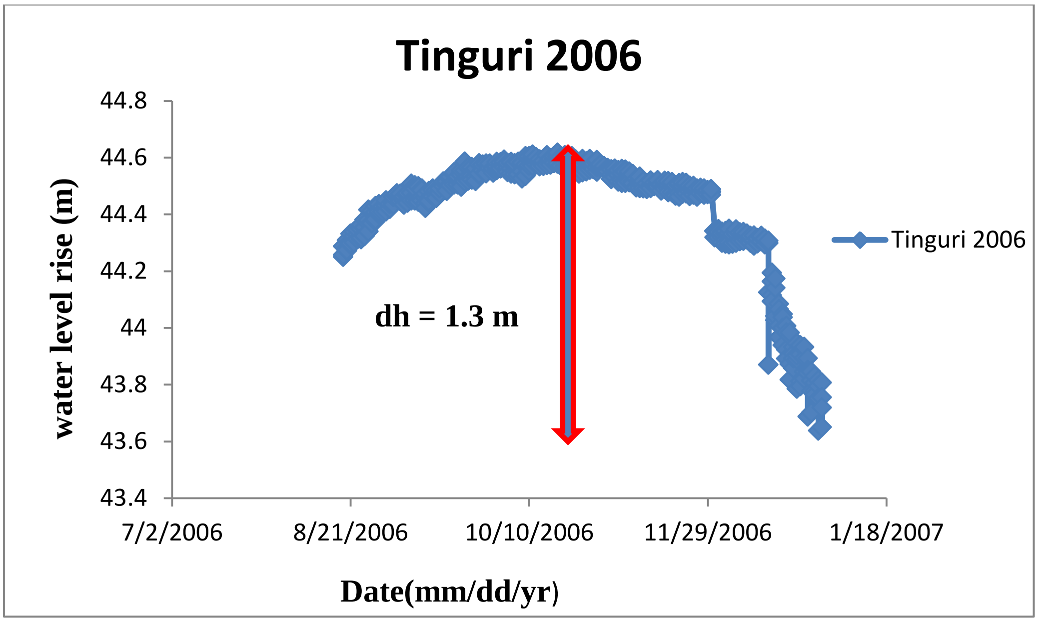


Figure 4.21. Groundwater hydrograph of well WVB12 in 2006

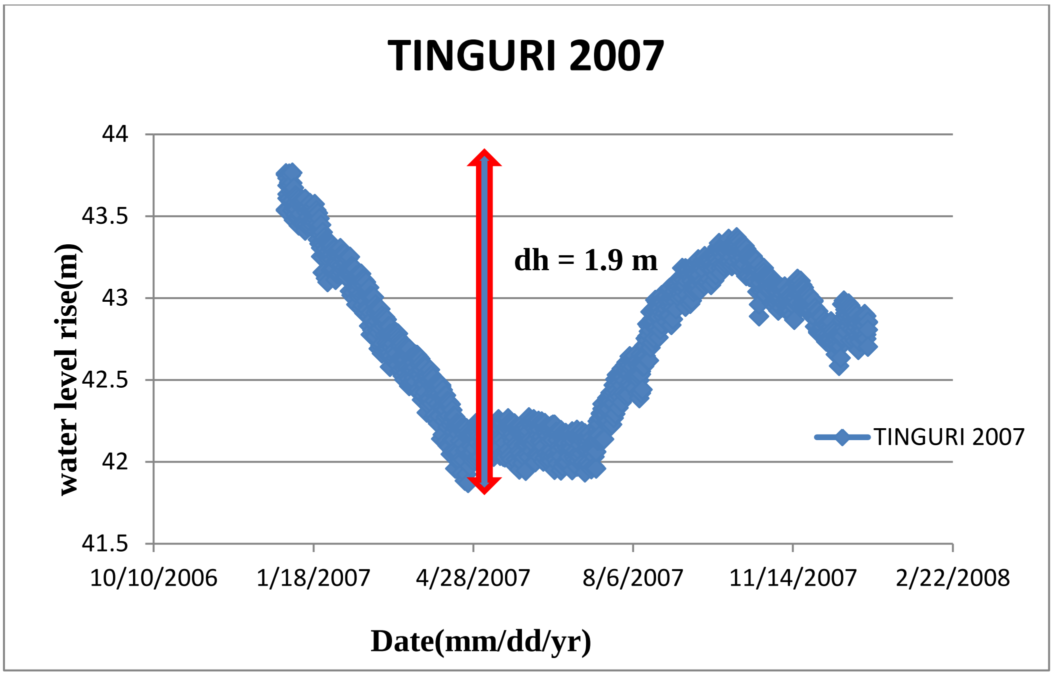


Figure 4.22. Groundwater hydrograph of well WVB12 in 2007

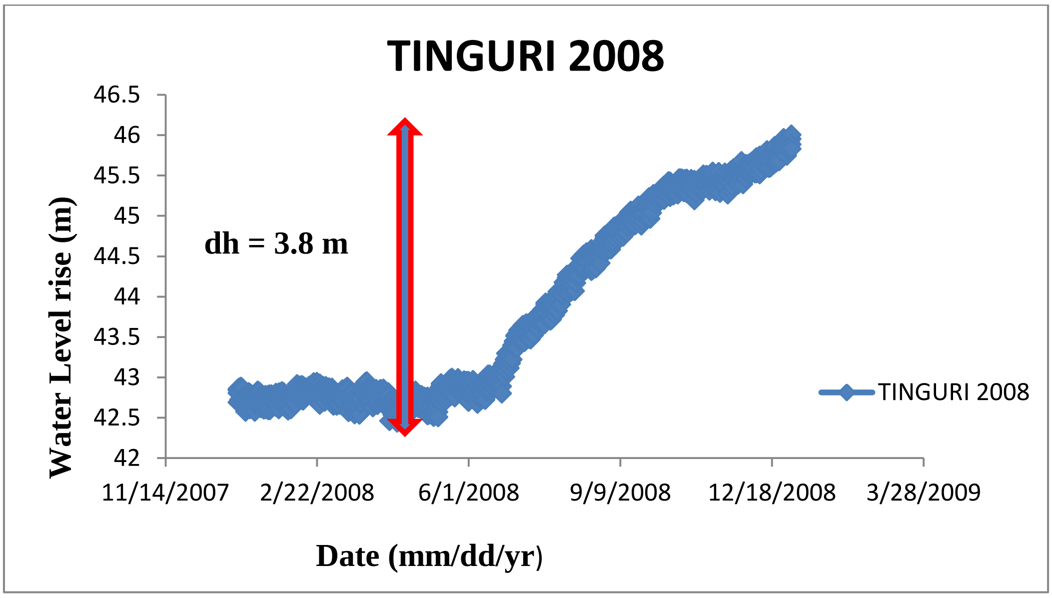


Figure 4.23. Groundwater hydrograph of well WVB12 in 2008

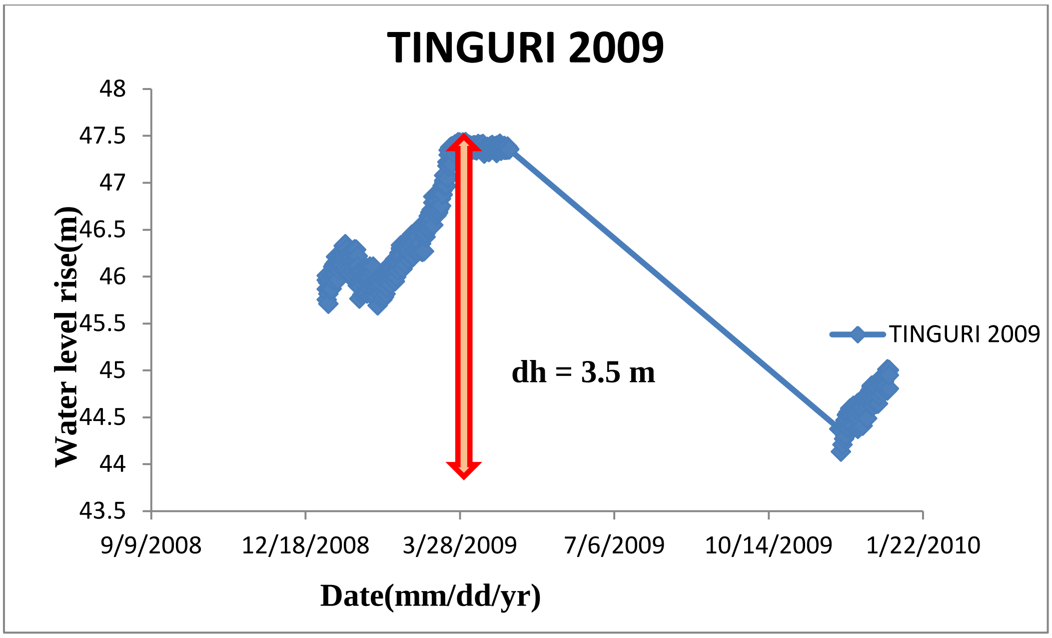


Figure 4.24. Groundwater hydrograph of well WVB12 in 2009

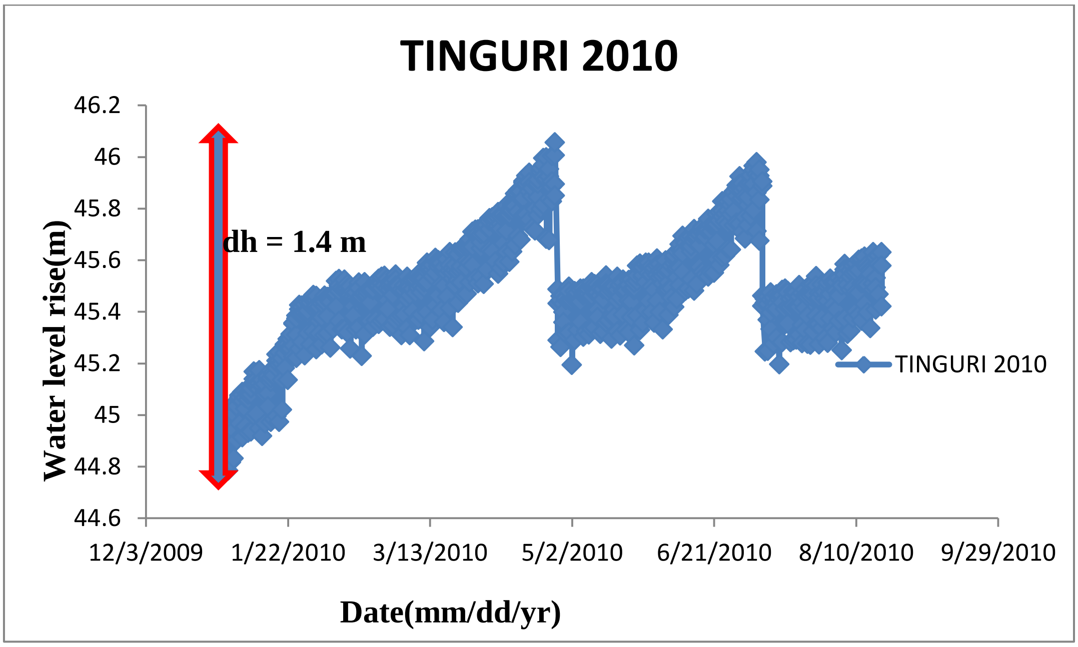


Figure 4.25. Groundwater hydrograph of well WVB12 in 2010

The hydrographs obtained for well WVB 13 (Figure 4.19 and 4.20) exhibit higher amplitude and sharper fluctuation than the hydrograph obtained for well WVB 12 (Figure 4.21 - 4.25). This may also be attributed to the thickness of the unsaturated zone. Shallow wells may recharge faster compared to deep wells and so the effect on the water level rise is quickly noticed leading to sharp amplitude of fluctuation.

Lee et al. (2005) confirms that amplitude of fluctuation during the monitoring period is partly related to the thickness of the unsaturated zone and the distance to the discharge area (main stream). Thus, thick unsaturated zone my lead to gradual peaking of the amplitude of fluctuation of the hydrograph for the monitoring period as compared to a shallow unsaturated zone whose amplitude will peak faster. This suggestion is justified because the depth to water for WVB 12 (100 m) is deeper than WVB 13 (51 m). Generally where the unsaturated zone is thick, the groundwater level changes smoothly (rise gradually) resulting in small amplitude, which can be observed in the hydrographs for well WVB 13. It further suggests that smoothing water-level rise may be as result of delayed drainage due to thick unsaturated zone.

The cumulative annual average of recharge estimation using WTF method was 7.14% and 8.1 % for the two wells (WVB 12 and WVB 13) respectively and its fall within the range of values obtained by the CMB method of about 0.4 % to 21 % of the annual rainfall, with an average of 8.9 %. The relatively lower estimated recharge values obtained from the WTF method compared with the CMB techniques might be due to few monitoring wells in the study area. Data from more monitoring wells evenly distributed in the area will help make better conclusions on spatial variation on the estimated recharge using WTF. CMB techniques applied in this study had quite good representation of data, thereby giving a relatively higher recharged rates compared with the WTF. The highly recharge areas from the CMB techniques were also attributed to open wells which are recharge directly from precipitation through runoffs. This may have also led to over estimation of recharge using the CMB techniques and might have slightly affects the average recharge rates.

Critical examination of the groundwater hydrographs and water level data of the two monitoring wells in the study area over the years suggests that recharge to groundwater in the area is almost entirely from the seasonal rainfall, since water level rise occurred mostly in the rainfall period. Spatial interpolation cannot be obtained from this study using the WTF method because of limited monitoring wells in the area.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

This study has shown that, the groundwater in the Gushiegu and surrounding areas did not exhibit much variation in the isotopic composition and its plots were scattered along the global meteoric water line (GMWL) and local meteoric water line (LMWL). This shows that the groundwaters in the study area is mainly meteoric and has undergone a slight primary evaporation. The relatively enriched nature of the groundwater compared to the rain water is attributed to the hard pan nature of the lithology of the area, leading to slow rate of recharge. The restricted vertical flow, due to low vertical hydraulic conductivities imposed by the clay fraction, limits vertical percolation and thus exposes the recharging rainwater to severe evaporation. The LMWL had a lower slope and d-excess values compared with the GMWL which suggest evaporation of rain drops leading to slight enrichment prior to recharge and might be due to amount and intensity of rainfall. The wider range of d-excess values for the rainwater samples further suggested that the samples were not taken under a homogenized condition at the sampling points but had individually been influenced by the prevailing environmental conditions at the time of sampling.

The EC (68.4 – 1114 μS/cm) values of the groundwater lends credence to the suggestion that groundwater is relatively fresh, indicating that it is quite recent. The relatively lower EC values means the water had not stayed in the aquifer for long to have dissolved enough solute in the groundwater. The CMB method estimated the groundwater recharge which ranged from 13.9 mm/y to 218 mm/y with an average of 89 mm/yr. This translates into about 1.3 % to 21.8 % of the annual precipitation in the area, with an average of 8.9%. It also means that averagely more than 90 % of the precipitations in the area are lost through evapotranspiration and runoff. The recharge distribution in the area based on CMB techniques does not show a distinct spatial pattern. Highly recharged areas were identified at the southwest and some part of the northeast of the study area based on the recharge prediction map. This was attributed to open well which gets recharge directs from precipitation and so might have not undergone much fractionation due to evaporation. It was further established that the highly recharge regions took their source from surface water (run off) prior to fractionation due to evapotranspiration. The WTF techniques based on all the assumptions made were used to estimates recharge rates over the years (7.14 % for WVB 12 and 8.1 % for WVB 13), which agrees with the values obtained by the CMB techniques.

Isotopic data of precipitation and groundwater were use to establish the possible relationship between groundwater and surface water in the partially metamorphosed sedimentary aquifer system in the Gushiegu area. Though, the data does not significantly establish potent relation between groundwater and surface water. The surface water in the study area has little or no interaction with the groundwater, this is established because the surface water were generally highly enriched compared to the groundwater, which might be due to evaporation as a result of kinetic fraction. Most of the surface water found in the area is in the forms of dams and ponds and due to the clayey nature of the soil, it is able to hold the surface water for a long time with little or no percolation.

5.2 Recommendations

The large population in the Gushiegu and surrounding areas depends basically on groundwater and sometimes surface waters for their domestic and commercial activities. To improve the socio-economic livelihood of the people the following recommendations are made:

- Proper management practice should be put in place to protect the recharge areas identified in the communities.
- Since the average annual recharge rate in these areas is very low and was observed that open wells were highly recharged due to direct precipitation, it is advisable, a deliberate construction of dugouts to be made in protected areas to encourage rapid recharge.
- Since most of the groundwater in and around the district are recharged by direct infiltration, good agricultural practices and proper sanitation measures must be encourages to protect the surface waters in the district from being polluted and further polluting the groundwater
- The “Special Well” as identified in this work did not exhibit any distinct characteristics from the groundwater in the area. To be able to understand the source and its formation scientifically, it is recommended that a thorough work be done solely on these wells in the area to help nullify the superstitious believe surrounding these wells.
- To be able to understand the processes and interpret the stable isotopic composition in surface waters (streams, river, lake, ponds) and groundwater, a Local Meteoric Line (LMWL) is needed. In view of this there should be an institutional collaboration to collect rainwater samples with a wide variation

across the country for a period of time (5 years) to help generate LMWL for districts to help in future interpretation of isotopes in future studies.

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APENDIX 1: Physical Parameters of Ground and Surface Water Samples.

SAMPLE ID	SOURCE	ELEVATION/m	Eh/mV	Ph	SALINITY	EC µS/cm	TDS/mg/l	DTW/m
GH 01	BH	200	-61.8	7.53	0.3	598	299	_
GH 02	SW	192	-23	7.41	0	69.1	34.5	_
GH 03	SW	179	-14.3	7.05	0.1	133.1	66.5	_
GH 04	SW	190	-13.7	7.04	0.1	151.9	75.9	_
GH 05	BH	202	-20.2	7.17	0.2	330	165	0.63
GH 06	BH	218	-67.4	8.1	0.4	747	373	_
GH 07	BH	208	-55.4	7.87	0.3	709	354	_
GH 08	SW	190	-31.5	7.4	0	90.1	45	_
GH 09	SP WELL	211	-4.9	6.86	0	68.6	34.2	1.6
GH 10	BH	234	-50.9	7.78	0.4	744	371	_
GH 11	BH	203	-56.7	7.9	0.2	510	255	_
GH 12	SW	222	-29.9	7.36	0	39.6	19.8	_
GH 13	BH	230	-49.7	7.76	0.2	412	205	_
GH 14	BH	195	-45.3	7.67	0.3	628	313	_
GH 15	SW	191	-32.2	7.41	0.1	149.3	74.6	_
GH 16	BH	178	-54.1	7.85	0.5	1019	508	_
GH 17	SW	219	-51.2	7.79	0.1	163.4	81.8	_
GH 18	BH	227	-31.3	7.39	0	79.7	39.5	_
GH 19	BH	228	-19	7.15	0.3	598	298	_
GH 20	BH	236	-58.1	7.92	0.3	546	272	_
GH 21	SW	223	9.6	6.58	0	34.6	17.2	_
GH 22	BH	223	-41.6	7.6	0.3	564	281	_
GH 23	BH	195	-50.1	7.76	0.4	747	373	_

CONTINUE:

SAMPLE ID	**SOURCE**	**ELEVATION**	**Eh/mV**	**Ph**	**SALINITY**	**EC/uS/cm**	**TDS/mg/L**	**DTW/m**
GH 24	BH	166	-50.8	7.78	0.4	895	444	_
GH 25	SW	147	-21.8	7.2	0	97.4	48.6	_
GH 26	SW	159	-19.5	7.16	0	114.8	57.5	_
GH 27	BH	158	-39.7	7.56	0.3	582	290	0.78
GH 28	BH	166	-50.4	7.77	0.3	654	326	4.22
GH 29	BH	164	-34.7	7.47	0.2	325	162.5	3.78
GH 30	SW	156	-21.2	7.19	0	63.6	31.7	_
GH 31	BH	171	-28	7.33	0.2	446	223	6.61
GH 32	SP WELL	168	-0.9	6.79	0	83.3	57.3	2.03
GH 33	BH	152	-16.4	7.09	0.2	364	181.3	1.58
GH 34	BH	153	-47.4	7.71	0.4	764	381	_
GH 35	SW	153	15.9	6.45	0.1	132.6	66.2	_
GH 36	BH	187	-30.3	7.37	0.5	1114	557	8.82
GH 37	BH	163	-41.7	7.6	0.3	624	312	_
GH 38	BH	184	-35.1	7.47	0.5	1079	537	1.52
GH 39	BH	182	-46.1	7.69	0.4	760	380	4.26
GH 40	BH	194	-29.8	7.36	1.2	0.00239	1194	2.88
GH 41	SW	187	-23.7	7.24	0.1	269	134.1	_

APPENDIX II: Chemical Parameters of Ground and Surface water Samples.

SAMPLE ID	OH-	Cl-	Ca 2+	Mg 2+	Na +	K+	HCO3-	NO3-	SO4 2-	PO4 3-	F-
GH 01	364	21.9	12.8	0.09	33.3	0	443.78	0.171	23.66	0.165	6
GH 02	48	6	3.2	0.19	11.3	11.4	58.52	0.107	12	0.062	0.9
GH 03	96	2	16	0.29	18	8.1	117.04	0.387	0.33	0.128	2
GH 04	92	6	9.6	0.33	23.1	16.2	112.16	0.079	0.33	0.159	2.1
GH 05	228	6	25.7	0.69	64.5	2.1	277.97	0.183	2.16	0.093	0.31
GH 06	440	140	9.6	0.02	460.8	0	536.43	0.095	5.83	0.054	2.08
GH 07	444	18	28.9	0.2	54.1	1.4	541.31	0.167	5	0.051	2.2
GH 08	64	6	12.8	0.24	21.5	4.1	78.02	0	13.66	0.093	0.28
GH 09	44	14	19.2	0.19	13.3	4.6	53.64	0.339	1	0.119	0.2
GH 10	476	14	41.7	1.23	13.1	4.3	580.32	0.019	6.66	0.099	0.65
GH 11	204	38	9.6	0.02	34.9	0	248.71	0.043	32	0.113	11.4
GH 12	48	6	6.4	0.1	9.6	2.3	58.52	0.047	0.33	0.113	0.16
GH 13	200	140	6.4	0.02	230.3	0	243.83	0.215	18.33	0.034	1.22
GH 14	392	14	38.5	0.64	260.7	0	477.91	0	7	0.190	1.6
GH 15	96	6	48.1	0.3	20.7	19.7	117.04	0.187	33.66	0.122	0
GH 16	612	140	32.1	0.48	760	1	746.13	0	18	0.065	1.4
GH 17	156	140	28.9	0.08	9.6	2.4	190.19	0	14.5	0.392	0
GH 18	44	6	16	0.06	9.9	3.5	53.64	0.039	0.33	0.039	0.13
GH 19	148	14	38.5	0.73	62.9	13	180.43	0.195	6.5	0.165	0.56
GH 20	396	10	35	0.18	290.8	1.6	482.79	0.839	0.33	0.102	0.84
GH 21	20	10	0.4	0.04	8.4	2.4	24.38	0	0.33	0.039	0
GH 22	354	10	159.9	0.22	310.1	6.7	468.16	0	0.33	0.059	0
GH 23	372	38	40.1	0.48	280.2	0	453.53	0.127	9.16	0.244	1.3

CONTINUE:

SAMPLE ID	**OH-**	**Cl-**	**Ca 2+**	**Mg 2+**	**Na +**	**K+**	**HCO3-**	**NO3-**	**SO4 2-**	**PO4 3-**	**F-**
GH 24	500	42	56.1	0.86	330.5	4	609.59	0.075	25	0.051	0.77
GH 25	92	10	20	0.18	13.9	11.3	112.16	0.019	6.5	0.045	0.2
GH 26	56	6	16	0.19	17.6	11.5	68.27	0.099	0.33	0.295	0.29
GH 27	37.2	10	40	0.81	230.9	3.8	453.53	0.083	2.16	0.102	0.32
GH 28	400	10	52.1	0.82	140.4	3.7	487.67	0	9.33	0.165	0.97
GH 29	176	30	48.1	0.6	48	4.5	214.57	0	0.33	0.019	0.31
GH 30	45	10	9.6	0.12	9.5	5.6	54.86	0.155	0.33	0.159	0.31
GH 31	260	18	38.5	0.87	80.7	7.6	316.98	0.071	1	0.068	0.55
GH 32	52	14	19.2	0.2	14.5	13.3	63.39	0.355	3	0.307	0.1
GH 33	244	10	83.4	0.61	23	15.8	297.47	0.123	0.33	0.401	0.28
GH 34	530	8	44	0.96	340.5	1.9	646.16	0.079	9.83	0.011	0.82
GH 35	100	8	19.2	0.3	21.3	4.2	121.91	0.143	0.33	0.048	0.16
GH 36	416	90	86.6	1.55	300.5	57.3	507.17	0.135	22.5	0.036	0.78
GH 37	360	34	67.3	1.04	115.8	2	438.90	0.111	14	0.085	0.62
GH 38	312	94	44.9	1.35	113.4	101.9	380.38	0.235	18.5	0.125	0.6
GH 39	364	140	51.3	1.23	85.6	61.2	443.78	0.143	12	0.110	0.67
GH 40	52	322	42.1	4.39	35.9	5.4	63.39	0.399	61.33	0.036	0.19
GH 41	148	26	22.4	0.43	41.1	9.9	180.43	0.091	9.83	0.039	0.37

APPENDIX III: Physical and Chemical Parameters of Rain Water Samples

SAMPLE ID	Ph	TEMPERATURE	EC	TDS	Cl^-
TM2-Cl	7.02	25.7	38	17.6	1.99
TM-07-Cl	6.28	25.2	3.1	1.5	0.99
TM-12-Cl	6.77	25.2	62.9	41.5	2
TM-09-Cl	6.29	25.4	7.29	3.6	1
TM-13-Cl	8.03	25.5	45.1	22	0.1
TM-5-Cl	5.99	25.5	20.6	11.3	0.99
TM-10-Cl	6.21	24.8	8.04	3.39	1.01
TM-1-Cl	6.4	25.5	36.1	17.7	1
TM-4-Cl	5.8	25.8	9.98	4.7	2
TM-14-Cl	6.51	25	37.7	17.5	1
TM-18-Cl	6.42	25.4	15.02	7.1	1.99
TM-16-Cl	6.37	25.4	16.11	7.2	1.99
TM-11-Cl	7.12	25.3	86.1	40.9	1

APPENDIX IV: Chloride-Mass Balance Estimation of Recharge

Sample ID	Cl- in GW	Average Cl- in RW	Conc. Fact.	Con. Fact. In %	Av. Ppt. mm/y	Amt. Rech. mm/y
GH 01	21.9	1.31	0.0598	5.982	1000	59.81
GH 05	6	1.31	0.2183	21.83	1000	218.33
GH 06	14	1.31	0.0936	9.357	1000	93.57
GH 07	18	1.31	0.0728	7.278	1000	72.77
GH 09	14	1.31	0.0936	9.357	1000	93.57
GH 10	14	1.31	0.0936	9.357	1000	93.57
GH 11	38	1.31	0.0345	3.447	1000	34.47
GH 13	14	1.31	0.0936	9.357	1000	93.57
GH 14	14	1.31	0.0936	9.357	1000	93.57
GH 16	14	1.31	0.0936	9.357	1000	93.57
GH 18	6	1.31	0.2183	21.83	1000	218.33
GH 19	14	1.31	0.0936	9.357	1000	93.57
GH 20	10	1.31	0.131	13.1	1000	131.00
GH 22	10	1.31	0.131	13.1	1000	131.00
GH 23	38	1.31	0.0345	3.447	1000	34.47
GH 24	42	1.31	0.0312	3.119	1000	31.19
GH 27	10	1.31	0.131	13.1	1000	131.00
GH 28	10	1.31	0.131	13.1	1000	131.00
GH 29	30	1.31	0.0437	4.367	1000	43.66
GH 32	14	1.31	0.0936	9.357	1000	93.57
GH 31	18	1.31	0.0728	7.278	1000	72.77
GH 33	10	1.31	0.131	13.1	1000	131.00
GH 34	8	1.31	0.1638	16.38	1000	163.75
GH 36	90	1.31	0.0146	1.456	1000	14.55
GH 37	34	1.31	0.0385	3.853	1000	38.52
GH 38	94	1.31	0.0139	1.394	1000	13.93
GH 39	14	1.31	0.0936	9.357	1000	93.57
GH 40	322	1.31	0.0041	0.407	1000	4.06

APPENDIX V: Stable Isotope Content of the Groundwater

SAMPLE ID	δ ^{2}H‰	δ^{18}O‰	d-excess(‰)
GH01	-25.95	-4.56	10.53
GH05	-16.82	-2.90	6.38
GH06	-32.82	-4.89	6.31
GH07	-20.39	-3.36	6.53
GH09	-7.49	-1.77	6.72
GH10	-18.96	-3.94	12.60
GH11	-27.14	-4.86	11.80
GH13	-26.85	-4.74	11.12
GH14	-21.19	-4.08	11.50
GH16	-17.39	-4.30	17.01
GH18	-13.43	-2.39	5.69
GH19	-18.33	-3.29	8.02
GH20	-32.76	-4.96	6.96
GH22	-33.38	-5.05	7.05
GH23	-24.59	-4.52	11.60
GH24	-19.85	-3.67	9.52
GH27	-16.72	-3.41	10.58
GH28	-22.72	-3.55	5.74
GH29	-15.83	-2.99	8.15
GH31	-22.21	-3.93	9.29
GH32	-21.26	-3.92	10.14
GH33	-15.96	-3.05	8.44
GH34	-22.00	-3.84	8.75
GH36	-20.12	-3.25	5.90
GH37	-22.85	-4.19	10.70
GH38	-16.89	-3.26	9.24
GH39	-19.46	-3.58	9.20
GH40	-13.89	-2.81	8.61

APPENDIX VI: Stable Isotope Content of the Surface Water

SAMPLE ID	δ 2H‰	δ ^{18}O‰	d-excess(‰)
GH03	2.41	0.35	-0.41
GH04	13.59	2.64	-7.55
GH08	6.60	1.07	-1.99
GH12	-6.37	-1.51	5.77
GH15	20.29	3.53	-7.98
GH17	-11.65	-1.92	3.73
GH25	14.66	2.16	-2.66
GH30	-4.96	-0.96	2.72
GH35	-1.40	0.016	-1.53
GH41	6.31	0.95	-1.29

APPENDIX VII: Stable Isotope Content of Rain Water.

Sample ID	δ2H‰	δ18O‰	d-excess(‰)
TM-06-1S	-57.50	-8.94	14.01
TM-07-1S	-61.47	-9.37	13.48
TM-1-1S	-67.40	-9.20	6.26
TM-2-1S	-67.67	-9.49	8.29
TM-3-1S	-73.85	-9.38	1.20
TM-4-1S	-57.62	-8.70	12.01
TM-5-1S	-79.18	-10.15	2.05
TM-08-1S	-56.17	-8.88	14.92
TM-09-1S	-48.89	-7.94	14.66
TM-10-1S	-50.97	-8.28	15.26
TM-11-1S	-43.55	-7.22	14.24
TM-12-1S	-12.18	-1.74	1.79

APPENDIX VIII: Table Showing the Estimated Recharge values using WTF

TINGURI (WVB 12)

Year	**2006**	**2007**	**2008**	**2009**	**2010**
∂H(mm)	1300	1901	3800	3500	1400
S_y	0.01-0.05	0.01-0.05	0.01-0.05	0.01-0.05	0.01-0.05
Recharge (mm/yr)	13-65	19-95.1	38-190	35-175	14-70
Mean Recharge (mm/yr)	39.0	57.1	114.0	105.0	42.0
% of Annual Rainfall	3.9	5.7	11.4	10.5	4.2

GALWEI (WVB 13)

Year	**2006**	**2008**
∂H(mm)	1400	4000
S_y	0.01-0.05	0.01-0.05
Recharge(mm/yr)	42.0	120.0
% of Annual Rainfall	4.20	12.0