

**USING HYDROCHEMICAL AND ISOTOPIC TRACERS TO ASSESS THE
IMPACT OF ANTHROPOGENIC ACTIVITIES ON GROUNDWATER
QUALITY IN BONGO AND KASSENA NANKANA WEST DISTRICTS IN
UPPER EAST REGION OF GHANA**

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BY

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DECLARATION

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DEDICATION

This work is dedicated to my parents, Mr. and Mrs. Dauda and my husband Musah Salifu for their support and prayer given me through this Programme

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To Allah (SWT), for giving me the strength and the opportunity to chase my dreams.

To my husband, Musah Salifu, thank you for your infinite patience and guidance.

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ABSTRACT

The population within Bongo and Kassena Nankana West Districts, in the Upper East Region of Ghana is estimated to be about 84,545 and 70,667, respectively. An estimate of about 80% of the population depends on groundwater for domestic and agricultural purposes. However, groundwater resources in the Districts is at risk due to anthropogenic activities such as rapid increase in irrigation activities and animals rearing, open defecation and uncontrolled disposal of animal droppings, improper land use, waste disposal, and illegal mining activities. This study was carried out to use hydrochemical and isotopic tracers to assess the impact of anthropogenic activities on groundwater quality in the study areas. The study employed hydrochemistry and isotopic techniques to assess the chemical quality of groundwater in the study areas. A total of sixty-four (64) boreholes were sampled from the study areas for the study. The samples were analysed in-situ for pH, conductivity and salinity using a HACH potable meter; and bicarbonate using a titrimetry. Analytical methods employed for the determination of major and minor ions were (Na^+ and K^+) complexometric titration (Ca^{2+}) and (F^- , Cl^- , NO_3^- , PO_4^{3-} , and SO_4^{2-}). Atomic absorption spectrometry was used for the determination of Mg^{2+} and heavy metals (Fe, Mn and As). Stable isotope of ^2H and ^{18}O composition of the water samples were determined using Liquid-Water stable isotope analyser [Off-Axis Integrated Cavity Output Spectroscopy (off axis ICOS) via Laser Absorption]. In general, majority of the ions are within the permissible limit for drinking purpose except few locations in the study areas. The Gibbs Diagram, the Piper Trilinear Diagram and the Hierarchical Cluster Analysis reveal different degrees of water-rock interaction or mineralization and are consequence of silicate weathering and silicate mineral dissolution, cation exchange and to a lesser extent

fertilizer application. Based on the Water Quality Index (WQI) classification, the majority of the samples fall under excellent to good water category and suitable for drinking water purposes, except for groundwater in few areas which showed deteriorating water quality. The stable isotopes composition implies, there has been fractionated before recharge . Since, the values deviate towards the positive values.

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LIST OF ABBREVIATIONS

| | |
|---------------|---|
| AAS | Atomic Absorption Spectroscopy |
| BWL | Borehole Water Evaporation Line |
| CA | Cluster Analysis |
| CBE | Charged-Balance Error |
| EC | Electrical Conductivity |
| EDTA | Ethylenediaminetetraacetic Acid |
| FAAS | Flame Atomic Absorption Spectroscopy |
| GGSD | Ghana Geological Survey Department |
| GIS | Geographical Information System |
| GMWL | Global Meteoric Water Line |
| GSS | Ghana Statistical Service |
| HCA | Hierarchical Cluster Analysis |
| HG-AAS | Hydride Generation Atomic Absorption Spectroscopy |
| LMWL | Local Meteoric Water Line |
| PCB | Precambrian Basement |
| TDS | Total Dissolved Solids |
| VSMOW | Vienna Standard Mean Ocean Water |
| WHO | World Health Organisation |
| mg/L | milligrams per litre |
| mL | millilitres |
| µS/cm | micro Siemens per centimetre |
| MPL | Maximum Permissible limit |

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of the Study

The survival of any living being depends on water as a life source. Apart from domestic use of water, it is essential for commerce, industry and agricultural purposes. Over the years, there has been increase in high demands of surface water due to urbanization and industrialization. Surface water in many parts of the world has deteriorated and polluted as consequence of unplanned housing in most cities, improper disposal of wastes, uncontrolled commercial and industrial operations, improper mining, migration of leachate from landfill sites and sewage and effluent leakage (Huan et al., 2013). As consequence of such degradation, many people rely on groundwater.

Historically, the rural communities in Ghana relied on raw surface waters for their water needs. These water resources turn out to dry during the dry seasons due to alteration in climatic patterns, depleting tree cover and irregularity of the rainfall patterns making it very difficult to access these waters throughout the year. In addition, as a result of surface runoff from agricultural activities and other anthropogenic activities, surface-water sources in these areas are often polluted and are sources of water related diseases in these communities (Akiti 1982). In the long term, the provision of groundwater resources has therefore become an alternative source of suitable water supply, since these groundwater resources are reliable, consistent, safe, and more importantly accessible to the people .

In Bongo and Kassena Nankana Districts, groundwater resource development contributes substantially to the socioeconomic livelihood of the people living in the areas. Groundwater besides being used for the domestic purposes, is also used for rearing of animals and irrigational purposes. This is probably due to the high percentage of rural population (scattered settlements) which is about 71.9 % of the regional population (GSS, 2013). Rapid rainfall seasons, and long dry seasons, makes communities to frequently experience inadequate surface water supply, hence, the choice to use groundwater (Ofosu, 2011).

Therefore, provision of groundwater for communities has resulted in borehole drilling activities increasing significantly in the study areas, generally funded through development aid (Martin, 2006) .

Kortatsi (1994), stated that the use of groundwater is the most cost-effective means of rural water supply. This is because in several areas of the country, groundwater can be tapped at shallow depths. Also, in many cases borehole yields are good and serve as adequate supply of water throughout the year (Gyau-Boakye and Dapaah-Siakwan. 2000) .

For both rural and urban population, groundwater is obviously a vital freshwater resource, hence its assessment estimation, sustainability and proper management is a major concern (Adomako, 2010).

However, groundwater resources in the Bongo and Kassena-Nankana West Districts is under threat as a result of increased population, rapid increase in irrigation activities and animals rearing, open defecation and uncontrolled disposal of animal droppings. Groundwater resources in the study areas experience localized water quality degradation due to high concentrations of pollutants such as fluoride (Dapaah-Siakwan et al., 2006), manganese, and iron (Carrier et al., 2009).

Studies have also revealed that frequent use of fertilizers by farmers can influence the chemical quality of groundwater. Nitrate levels in groundwater measured in 1977 in the Upper Region although they were low, show a substantial increase in 1980. This was as a result of frequent use of fertilizers by farmers in the area (Akiti, 1982) . An estimate of about 80 percent of the population depends on groundwater. This means increase in population without corresponding increase in the number of boreholes resulting in over exploitation of the groundwater due to many people depending on the fewer boreholes. Hence, the need to understand the chemical composition of groundwater and the origin.

The human health impact that are caused by ingestions of contaminated groundwater can be acute, subchronic and chronic. Contaminated surface water can over time cleanse itself or be treated but once groundwater is polluted, to find a cure for what is already in the ground is much harder. To efficiently and sustainably make use of groundwater, it is important to preserve and evaluate groundwater quality.

Gibbs plots, multivariate statistical tools, Piper diagram and bivariate plots will be used to understand the chemical processes and anthropogenic impacts in the areas based on hydrochemical data generated from the study. Moreover, environmental isotopes would be used as a supplementary tool to understand hydrological processes like, direct percolation, evaporation effect and selective infiltration taking place in the study area .

1.2 Statement of the Problem

Anthropogenic activities (improper irrigation activities and animals rearing, open defecation and uncontrolled disposal of animal droppings, improper land use, waste disposal, and as well as illegal mining activities) are growing concern for many communities in the world and has become problematic particularly to communities that depend heavily on the fresh groundwater resources for their livelihood. The people of Bongo and Kassena Nankana West Districts in the Upper East Region of Ghana are no exception as their very existence is being threatened by anthropogenic activities.

A consequence of Anthropogenic activities, is the deterioration in the quality of the groundwater rendering the resource unsuitable for use and impacts the socio-economic wellbeing of these communities. The anthropogenic activities can affect the quality of the otherwise good quality freshwater that these communities relied on for irrigation of vegetables and grains and other conjunctive uses This does not only have serious implications for food security and sustainable livelihood for the community alone but on the populace in Northern Ghanaian and the sub-region as these vegetables and grains are produced year-round and exported to neighboring countries.

Even though, high NO_3^- and F^- levels have also been reported in the areas by earlier workers (Akiti 1980; Apambire et al. 1982), this project is thus crucial in that it will investigate the impact of anthropogenic activities on the quality of the groundwater using hydrological and isotopic tools and will eventually help advice sustainable development and management of groundwater resources leading to variations in irrigation policies and practices, thus facilitate sustainable groundwater abstraction under climate change conditions for the vulnerable communities in the Districts.

Not only will it guarantee the water security of future domestic, agricultural and industrial water needs of the people but will complement global effort to eradicate hunger and unemployment by using the groundwater for large scale irrigation activities. This will lead to an improved productivity in terms of crop yield and quality, better nutrition and improved livelihood. With increased crop yield, comes food security and better economic empowerment of these vulnerable communities, as they will have more food to sell unto the market.

1.3 Objectives

The objective of the study is to use hydro chemical and isotopic tracers to assess the impact of anthropogenic activities on groundwater quality. The specific objectives are,

- To identify the hydro-chemical processes that account for the chemistry of the groundwater.
- Assess the general groundwater quality in the study areas and compute the water quality index.

- Assess the influence of anthropogenic activities on groundwater quality in the study area.
- Trace the origin of the groundwater .

1.4 Justification

Agriculture is the major occupation of the people of Bongo and Kassena Nankana West Districts, representing 72.6% and 81.0% respectively according to (GSS, 2014). This means that there is a high demand on groundwater supply for irrigation and rearing of livestock during the dry season since the surface water turn out to dry up. Hence, knowledge from the study would serve as a source of information on how the consumers can use such waters .

Again, besides the agriculture used of groundwater, its domestic use is also increasing because according to GSS (2014) the Bongo District has a population of 84,545 and the Kassena Nankana District has a total population of 70,667, representing an increase of 8.6 percent of its population in the 2000 PHC (77,885). Therefore, the study is needed to plan for a long-term supply of good quality water for the residents of the two areas under study. Moreover, the success of the study will provide groundwater quality information for managing anthropogenic activities to prevent future contaminations .

In addition, the geochemical and isotopic tools would provide a better understanding of the origin and condition of the groundwater in the two areas. Lastly, the result of this

research will provide the necessary tools for all stakeholders in the water industry, to properly monitor groundwater resources to meet water demands challenges now and future.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Geochemical Studies

Geochemical and hydro chemical studies play vital roles in understanding the controls of groundwater quality. The factors that mainly influenced quality of groundwater are rock chemistry in recharge areas, different geochemical processes occurring within the aquifer, and anthropogenic activities. (British Geological Survey, 2000; Chilton, 1996; Fadaei and Sadeghi, 2014; Fathy et al., 2012; Gibrilla, 2010a; Izzat et al., 2013; Kumar et al., 2011) .

Groundwater quality is also controlled by anthropogenic activities, decay of organic matter, ion exchange reactions, weathering and dissolution of minerals, evapotranspiration and evaporation, mixing of different water qualities, and selective uptake of ions by vegetation, (Appelo and Postma, 1996b) .

Geochemical studies profoundly provide key understanding of pollution that originates from natural and anthropogenic sources and knowledge on migration of elements in and between different environmental compartments, and distribution (Gałuszka and Migaszewski, 2012). This is very significant should there be pollution increase in the future .

In groundwater studies, however, the key issues of geochemical studies include finding anomalies resulting from geogenic and anthropogenic activities, origin and evolution of the groundwater etc. The integrated use of geochemical methods has proved to be an

effective approach for investigating the evolution and movement of groundwater (Adomako et al., 2010; Bath and Strömberg, 2004; Edmunds et al., 2003; 2002; Trevor, 1990) .

Various studies on ground water chemistry have revealed that either some or all of the above-mentioned factors influence the chemistry of groundwater. In Upper East region, quite a number of studies have been conducted on the geochemistry and stable isotopes compositions, biological and chemical quality of groundwater. Among them are; Akiti (1982); Apambire et al., (1997); Oyelude et al., (2013); Pelig-Ba, (1998); Smedley et al., (2002); and Tiimub and Forson, (2008) .

Akiti (1982) investigated Nitrate levels in Upper region of Ghana. In his research, nitrate level of shallow groundwater > 30 m measured in 1977 and 1980 were low but showed a significant increase within the three years' period. The increase and source of Nitrate was attributed to animal excrements resulting from cattle rearing and agricultural fertilizers .

In Upper Region of Ghana, fluoride distribution in relation to the geology, genesis, and the geochemistry, and health implications has been studied (Apambire et al., 1997). The fluoride levels in the groundwater ranged from 0.11 to 4.60 ppm in their study. The fluorine-enriched Bongo coarse-grained hornblende granite and syenite suite had the highest concentrations. Within the Bongo granitoids, clay products from anion exchange with micaceous minerals and the dissolution of the mineral fluorite were the sources of groundwater fluoride.

Pelig-Ba (1998) analysed water samples from 60 boreholes located in the Upper East and West Regions of Ghana for 20 trace elements. He reported that, the concentrations of most of the trace elements were higher as compared to their concentrations in natural water systems. Fe, Mn, Al, Sr, Ba and Zn were elements with excessively high concentrations, compared to WHO drinking water guidelines. The local bedrock is the dominant source of the trace elements that resulted in the existences of these trace elements in the analysed water samples .

Adetunde and Glover, (2010) research reported that boreholes located in unsanitary environment (ie) near septic tanks were found to have high coliform bacteria counts .

Kubreziga, (2012) investigated the risk of infant methemoglobinemia (a condition that result from exposure to high nitrate concentration) in Upper East region. In his research, nitrate levels for about 43 % of underground water sources were above accepted limits . About one (1) out of every twelve (12) children stands the risk of being exposed to methemoglobinemia when using unregulated water sources; 0.08 of the children was found to be at the risk of being exposed to methemoglobinemia .

In Gushegu District of Northern Region, Salifu et al., (2015) used 7 rock samples and 19 groundwater sampling points to estimate the origin of the groundwater, water types, water quality, and sources of various ions. He reported that the groundwater chemistry from the area is Na–Ca–Mg–HCO₃ and Na– HCO₃ water type and was generally influence by rock weathering and precipitation. Also, the study reported that, most of the groundwater are of

meteoric origin with some showing considerable evaporation before recharged, and 53 % of the groundwater samples are of poor quality due to high F^- concentrations ($> 1.5 \text{ mg/L}$) .

Bakobie and Awal (2015) used 10 hand-dug wells to investigate the groundwater quality in Janga, West Mamprusi District, based on the parameters; pH, EC, TDS, NO_3^- , PO_4^{3-} , Cl^- , F^- , SO_4^{2-} , Faecal coliform and *E. coli*. The study suggested that although chemical parameters were below WHO recommended guideline for drinking water, coliform bacteria were above WHO limits; hence it is unsuitable for direct human consumption.

Rossiter et al., (2010) used 260 wells and boreholes to evaluate the chemical water quality in Ghana. 38 percent of the samples having high concentrations of inorganic pollutants that exceed the WHO guidelines. The study identified major problems to be high concentrations of NO_3^- , F^- , Al and Cl, low pH, high turbidity, and in localized areas, B, As, U and Pb. Their study recommended the need for monitoring of groundwater sources .

2.2 Groundwater Quality

Zuane, (1990) stated that, chemical solution which is generally dilute and really a complex can be to describe groundwater. The minerals dissolution in the rock and soil with which it is or has been in contact mainly produce the chemical composition of groundwater. The geochemistry of the soil through which the water flows prior to attainment the aquifers mostly affect the type and extent of chemical contamination of the groundwater.

Numerous factors that result in groundwater chemical alteration are; anthropogenic impacts, residence time of groundwater, interaction with solid phases, mixing of groundwater with pockets of saline water and as well as seepage of polluted runoff water, (Stallord and Edmund, 1983; Dethier, 1988; Faure, 1998; Umar and Absar 2003; Umar et al., 2006) .

Lewis et al., (1982) indicated that, the natural state of groundwater is generally of good quality due to soil and rocks which act as filters. However, human excreta containing pathogens such as viruses and bacteria small enough to diffused through the aquifer and the soil medium to groundwater bodies, because not all soils are equally effective in acting as filters.

In regions with little soil cover where hard solid rocks emerge at the ground or close to the surface, rainfall contributes substantial amounts to some elements in groundwater. The dissolution of minerals continues as water flows through the ground and with the length of the flow path, the concentration of dissolved elements tends to increase. Groundwater is saline, with concentrations reaching up to ten times the salinity of the sea where the rate of flow is extremely slow at excessive depths.

Groundwater when polluted can no longer be safe for drinking and unsuitable for its purposes. Particularly in a fractured aquifer where the material above the aquifer is permeable, pollutants can leak into groundwater. The lack of accessibility of clean water,

particularly during the dry season which has subsidiary effects on the human health is the major issue in both Bongo and Kassena Nankana Districts. High fluoride concentrations are one of these pollutants, particularly in groundwater from boreholes even though dug wells, rivers and reservoirs can also give high concentrations of fluoride .

However, not every borehole yields high-fluoride waters and therefore wells used for drinking water must be tested. (Smedley, et al., 2002)

The presence of high-nitrate concentrations in some of the boreholes in the study areas is as result of anthropogenic impact on the groundwater, (Anku Yvonne, et al., 2008)

2.3 Water Quality Index (WQI)

The intricate process of assessing water quality has been ease into a single parameter called water quality index, a tool which reduces the large number of data into single value and makes information easily and rapidly understood by the layman (Tomer, 2015). Water quality index (WQI) is a dimensionless value and combines multiple water-quality factors into a single number and aids in interpreting the quality of water as a single numerical value (Horton, 1965) .

Most commonly used water quality index are; Canadian Council of Ministers of Environment (CCMEWQI), National Sanitation Foundation (NSFWQI), British Columbia (BCWQI), Oregon (OWQI), Overall Index of Pollution (OIP), Bhargava method, Smith 's index, The River Ganga Index, Tiwari and Mishra index, and Stigter index (Tomer, 2015).

Extensive review on the various water quality index for surface water are given in Bharti and Katyal (2011) and for groundwater are given in Tomer (2015) .

Currently, many researchers employ integrate advance statistics and GIS with water quality indices to delineate water quality in their study Tomer (2015) .

In Ghana, Gibrilla et al., (2011) used Water Quality Index (WQI), multivariate statistic and geostatistics to assess the suitability of groundwater for drinking, as well as groundwater quality for irrigation in Densu River basin. The study showed that groundwater quality varied as "excellent" and "good" water quality. Also, cluster, principal component analysis and geostatistics showed areas with potential deteriorating water quality .

Additionally, chemical indices like percentage of sodium (Na%), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), and permeability index (PI) indicate that the groundwater in the study area are suitable for irrigation. However, factor controlling groundwater quality was suggested to be the geology, as the main source of dissolved ions, and anthropogenic contributions in some areas .

In the Upper East Region of Ghana, Boah et al., (2015) have applied Water Quality Index (WQI) to assess suitability of the Veve Dam for drinking purposes. Ten (10) physico-chemical parameters, namely pH, Electrical Conductivity, Total Dissolved Solid, Total

Hardness, Nitrates, Sulphates, Chlorides, Calcium, Dissolved Oxygen and Biochemical Oxygen Demand were used for the assessment. The weighted arithmetic index method calculation of the WQI used was found to be 54.21 indicating poor quality .

2.4 Physio-Chemical parameter for water quality

The dissolved elements in groundwater, including magnesium, calcium, sodium, potassium, bicarbonate, sulphate, chloride and nitrite occur in the form of electrically charged ions. Various further account for insignificant elements of groundwater. Manganese, fluoride, and iron are trace elements which may be found in groundwater .

2.4.1 Electrical Conductivity

Electrical Conductivity is the ability of water to conduct an electric current; it is sensitive to variations in dissolved solids, mostly minerals salts (Hill, 2000). Electrical conductivity relates to total dissolved solids by a multiplication a factor commonly between 0.55 and 0.75. It has been reported that, a multiplication factor closes to 0.67 is usually for waters in which Na and Cl ions dominate, and higher for waters containing high concentration of SO₄. The conductivity of freshest water ranges from 10 to 1000 μ S/cm. Electrical conductivity have been used in some studies to establish a pollution zone (Chapman and Kimstah, 1996) .

2.4.2 Hardness

Hardness is a property of water that determines its ability to easily form lather with soap. Total hardness is directly related to the concentrations of calcium and magnesium.

Iron and manganese in ground water originate when water gets into contact with mineral groups and the weathering product that contain iron or manganese. Their concentrations can also be affected by wastewater from chemical industries. Excessive amount of iron and manganese are objectionable for both domestic and industrial water supplies because of their tendency to stain laundry and plumbing fixtures .

2.4.3 pH

The pH is a measure of the acid balance of a solution at a given temperature (Hill, 2000). pH measures the acidity or alkalinity of the (Davis and DeWiest, 1966). pH is controlled by the dissolved chemical compounds and biochemical processes in the solution. In unpolluted waters, pH is principally controlled by the balance between CO_2 , CO_3 , and HCO_3 ions as well as compounds such as fulvic acid and humic (Chapman and Kimstash, 1996). The pH of most natural waters ranged between 6.0 and 8.5, lower values can occur in dilute waters high in organic content .

2.4.4 Calcium

Calcium is present in all waters, for it readily dissolves from rocks rich in calcium minerals (Ca-feldspar, pyroxene, amphibole) (Appelo and Postma, 1996b; Chapman and Kimstash, 1996). Calcium concentrations in natural waters are generally < 15 mg/L. However, it may reach concentrations of 30 - 100 mg/L for waters associated with gypsum and carbonate-rich rocks like dolomite and calcite (Chapman and Kimstash, 1996) . In streams, carbonate minerals are the chief source of Ca and contribute about 80% or more on a global scale (Garrels, 1975). Only about 10 percent of Ca in the average stream is

derived from silicate minerals, and about the same or less is derived from sulphate (Garrels, 1975). Research has shown that other sources of calcium in groundwater arises from anthropogenic activities such as application of $\text{Ca}(\text{NO}_3)_2$ fertilizers (Stigter et al., 2006) .

2.4.5 Potassium

Potassium is found in low concentration in natural waters since rocks which contain potassium are relatively resistant to weathering (Chapman and Kimstach, 1996). However, it mostly enters into fresh water from industrial discharge, run-off from agricultural land and from weathering of K-feldspar and biotite silicate minerals (Appelo and Postma, 1996d). Concentration in natural waters are usually low (<10 mg/L) (Chapman and Kimstach, 1996), whereas concentrations as high as 100 and 25,000 mg/L can occur in hot springs and brines, respectively. However, high concentration of dissolved K in groundwater may occur where there are not sufficient alumino-silicate to fix it (Garrels, 1975) .

2.4.6 Sodium

Sodium is one of the most abundant elements on earth. Generally, increased concentrations in surface waters may arise from sewage and industrial effluents. In coastal areas, sea water intrusion can also result in higher concentrations. In groundwater, sources of increased concentration of sodium are the atmosphere, feldspar, rock-salt (halite), zeolite, and mirabilite (Appelo and Postma, 1996b) .

2.4.7 Magnesium

Magnesium is common in natural waters as Mg^{2+} , and along with calcium. It principally arises from the weathering of silicate rocks containing ferromagnesium minerals, biotite, pyroxene and amphibole (Appelo and Postma, 1996d), and from some carbonate rocks example dolomite and magnesite minerals (Appelo and Postma, 1996a) . It can also occur in many organometallic compound, organic matter, and clay minerals as a result of oxidation of abundant pyrite in organic-rich shales (Garrels, 1975). Natural concentrations of magnesium in fresh waters may range from 1 to > 100 mg/L, depending on the rock types within the catchment. Mg in groundwater may be controlled by montmorillonite formation in neutral or alkaline water, likewise the formation of dolomite (Garrels, 1975) .

2.4.8 Bicarbonate

Bicarbonate content in natural water arise from soil CO_2 pressure (atmosphere and biological respiration) and weathering (Appelo and Postma, 1996b; Chapman and Kimstach, 1996). In groundwater, weathering of rocks in areas of non-carbonate rocks, carbonate and bicarbonates concentrations in groundwater arise when dissolved CO_2 in rainwater passing soil becomes enriched in biogenic CO_2 decomposes and dissolves silicates, olivine, orthoclase, mica and clay minerals (Mazor, 1975; Hill, 2000) . In carbonate rocks, dissolution of calcite and dolomite are the primary source of bicarbonate ions in groundwater (Chapman and Kimstach, 1996; Mazor, 1975) .

2.4.9 Chloride

Most chloride occurs as chloride in solution and enters surface waters with the atmosphere deposition of oceanic aerosols, weathering of some sedimentary rocks (halite, sylvite) agricultural and road run-off (Benedict et al., 2003) . In pristine freshwaters chloride concentrations are usually lower than 10 mg/L and sometimes less than 2 mg/L. In arid and wet coastal areas, higher concentrations can occur near sewage and other waste outlets, irrigation drains, salts water intrusions (Chapman and Kimstash, 1996) .

Chloride is frequently associated with sewage, it is often incorporated into assessments as an indication of possible faecal contamination or as a measure of the extent of the dispersion of sewage discharges in water bodies (Benedict et al., 2003; Chapman and Kimstash, 1996) .

2.4.10 Sulphate

Sulphate is naturally present in surface waters as SO_4^{2-} , it arises from the atmospheric deposition of oceanic aerosols and the leaching of sulphur compounds, either sulphate minerals such as gypsum or sulphide minerals such as galena (PbS), sphalerite (ZnS), matte (CuFeS₂), pentlandite [(NiFe)₉S₈], and pyrite, epsomite, mirabilite, from sedimentary rocks (Appelo and Postma, 1996a, 1996b; Benedict et al., 2003; Chapman and Kimstash, 1996)”. It is the stable, oxidised form of sulphur and is readily soluble in water. Sulphate can be as an oxygen source by bacteria which convert it to hydrogen sulphide under anaerobic conditions. Sulphate concentrations in natural waters are usually between 2 and 80 mg/L, however, they may exceed 1000 mg/L near industrial discharges and in arid

regions where sulphate minerals, such as gypsum, are present (Chapman and Kimstash, 1996) .

2.4.11 Fluoride

Fluoride originates from the weathering of fluoride-containing minerals [amphiboles (hornblende), apatite, fluorite, mica] and enters surface waters with run-off and groundwaters through direct contact (Chilton, 1996). Fluoride mobility in water depends, to a large extent, on the Ca^{2+} ion content, since fluoride forms low solubility compounds with divalent cations. Other ions that determine water hardness can also increase F^- solubility. Fluoride concentration vary from 0.05 to 100 mg/L, however, in most situations they are less than 0.1 mg/L, and in groundwater concentration can be as high as 10 mg/L. Fluoride levels in groundwater exceeding the WHO guideline value of 1.5 mg/L (WHO, 2004) have been encountered in volcanic aquifers and lakes in the East African Rift systems (Chapman and Kimstash, 1996), sedimentary and metamorphic rocks in Ohio, Sri Lanka, India, Malawi and Tanzania (Chapman and Kimstash, 1996), and in granites aquifers in Ghana and Tanzania (Smedley et al., 2002) .

2.4.12 Phosphorus

Phosphorus is an essential nutrient for living organisms and exists in water bodies as dissolved (phosphates) and particulate species. Phosphates concentrations are expressed as mg/L. PO_4^- arise in natural water mainly from the weathering of phosphorus-bearing rocks and decomposition of organic matter. However, domestic wastewater (particularly those containing detergents), industrial effluents and fertiliser run-off contribute to elevated

levels in surface waters (Chapman and Kimstach, 1996) . Phosphorous is rarely found in high concentrations in freshwaters for it is actively taken up by plants. However, phosphorus ranges from 0.005 to 0.020 mg/L PO_4^- in some pristine waters and as high as 200 mg/L PO_4^- in some enclosed saline waters (Chapman and Kimstach, 1996) .

2.4.13 Nitrate

Generally, chemicals occurring in drinking-water are of health concern only after extended exposure for years. The only exception is nitrate. Nitrate and nitrite in water has been associated with methemoglobinemia, especially in bottle-fed infants. With a methaemoglobin level of 3-15%, skin can turn to pale grey or blue. Nitrate may arise from the excessive application of fertilizers or from leaching of wastewater or other organic wastes into surface water and groundwater (WHO, 2006) .

The nitrite ion contains nitrogen in a relatively unstable oxidation state. Chemical and biological processes can further reduce nitrite to various compounds or oxidize it to nitrate (Anon, 1987). Because of its solubility and its anionic form, nitrate is very mobile in groundwater (Fytianos and Christophoridis, 2003). It tends not to adsorb or precipitate on aquifer solids (Hem, 1985) .

2.5 Trace element parameter of water quality

Trace elements are generally present in small concentrations in natural water systems.

Their occurrences in groundwater and surface water can be due to natural sources such as dissolution of naturally occurring minerals containing trace elements in the soil zone or the aquifer material or to human activities such as mining, smelting of ores and improper

disposal of industrial wastes (Lowe, 1970). The trace metals in water behave in a typical manner. No single mechanism is sufficient to explain the processes that are undergoing in the water (Sudhira and Kumar, 2000) .

Trace metals such as Fe, Mn, As etc, are very important for the proper functioning of the biological system and their deficiency or excess in the human system can lead to number of disorders. Other trace metals like Pb, As, Hg etc. are not only biologically non-essential but definitely toxic (Sudhira and Kumar, 2000).

Copper and Fe are mixed in groundwater by rocks bearing iron and copper bearing ores via; cuprite, melakite, azurites, hematite, magnetite and iron pyrite. Iron in surface water is generally present in the ferric (Fe III) state (Mohapatra and Singh, 1999) . Concentrations of Fe greater than 1mg/L have been reported to occur in groundwater. The average daily requirements of iron are considered to be 10 mg.

Manganese plays a role in the proper functioning of flavoproteins and in the synthesis of sulphated mucopolysaccharides, cholesterol, haemoglobin and in many other metabolic processes (Bowen, 1972). Leaching of zinc from galvanized pipes, brass and zinc containing fittings plays a serious role in groundwater pollution, but in required quantity it is very essential for human metabolism. Dye and tannery industries pollute the water through chromium and other harmful chemicals (Bowen, 1972) .

2.6 Groundwater pollution

The suitability of water for various uses depends on the type and concentration of dissolved minerals and groundwater is reported to be composed of more dissolved minerals than surface water (Mirabasi et al., 2008).

Groundwater quality reflects inputs from the atmosphere, soil and water rock interactions as well as pollutant sources such as mining, land clearance, agriculture, acid precipitation, and domestic and industrial wastes (Appelo and Postma, 1993; Zhang et al., 2011) .

The quality of groundwater is constantly changing in response to daily, seasonal and climatic factors. Continuous monitoring of water quality parameters is highly crucial because change in the quality of water has far reaching consequences in terms of its effects on man and biota (Mirabasi et al., 2008).

Natural geochemical and biochemical, as well as anthropogenic impact on groundwater, do not only threaten the quality of human health but also poses a threat to sustainable development and management of groundwater resources (Appelo and Postma, 1993) .

Gibbs (1970) proposed that rock weathering, atmospheric precipitation, evaporation and crystallization control the groundwater hydrochemistry. Apart from natural factors influencing water quality, human activities such as domestic and agricultural practices impact negatively on groundwater resources.

Pollution of water bodies as a result of metal toxicity has become a source of concern among consumers. This concern has become alarming in response to increasing knowledge on their toxicity to human health and biological system (Anazawa et al., 2004) .

Generally, areas that are replenished at a higher rate are generally more vulnerable to contamination than those replenished at a lower rate. Large fractures in bedrock also contribute to contamination by providing a pathway for the contaminants (Palaniappan et al., 2010)

All-natural waters contain many dissolved substances. Contaminants such as bacteria, viruses, heavy metals, nitrates and salts have polluted water supplies as a result of uncontrolled human activities and untreated industrial waste discharges (Singh and Moseley, 2003) .

Groundwater resources in Bongo and Kassena Nankana area is under threat as result of increasing populations, inappropriate disposal of domestic waste and runoff from agricultural farms . Again Akiti (1980), stated that groundwater quality at the areas can deteriorate after prolong extractions. Studies have also revealed that frequent use of fertilizers by farmers can influence the chemical quality of groundwater (Akiti, 1982).

Water quality complaints have been used to monitor treatment operations and quantify the extent of distribution and water quality problems (Dietrich, 2006; McGuire, et al, 2005; Khiari et al., 2002; Burlingame and Anselme, 1995) .

Most studies linked the physico-chemical quality of groundwater to health. However, there seems to be a gap between groundwater quality and its effect on distribution systems and consumer complaints. Research has shown that rural water wells are not tested as suggested by professionals and are contaminated with pathogens and chemical from various sources (Charrois, 2010) .

Others have shown that, 33 percent documented outbreaks of water-related infections could be attributed to groundwater systems (Reynolds et al., 2008).

2.7 Environmental isotopes studies

Environmental Isotopes may be defined as those isotopes, both stable and radioactive, occurring in the environment in varying concentrations over which the investigator has no direct control (Fontes and Edmunds, 1989). Environmental isotopes generally used in hydrology are stable isotopes (deuterium, oxygen-18, and carbon-13) and radioisotopes (tritium and carbon-14) (Fontes and Edmunds, 1989). Environmental isotopes are imperative in tracing groundwater provenance, recharge processes, geochemical reactions and reaction rates (Clark and Fritz, 1997) .

2.7.1 Stable isotopes

Stable isotopes of water, oxygen-18 (^{18}O) and deuterium (^2H), are affected by meteorological processes that offer a characteristic pattern of their origin (Fontes, 1980; Gat, 1981). This pattern forms the basis for studying the provenance of groundwater. It

thus follows that waters from different sources or those exposed to different procedures such as evaporation and mixing, often acquire recognizable isotopic contents which aid as natural tracers (Dassi et al., 2005).

The evolution of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ composition of meteoric waters initiates with the evaporation from the oceans (IAEA, 1983, Faure, 1986, Fritz and Fontes 1980; Mazor, 1991). Deuterium-2 and oxygen-18 arise in the oceans in concentrations of about 310 ppm and 1990 ppm for molecular species H^2HO and $\text{H}^2\text{ }^{18}\text{O}$, respectively. The varying concentrations of these isotopes in natural waters can be measured in an isotope ratio mass spectrometer and are expressed in the delta (δ) notation as follows:

$$\delta = \frac{(R_s - R_{\text{std}})}{R_{\text{std}}} \times 1000$$

Where R_s = the isotope ratio ($^2\text{H}/^1\text{H}$, $^{18}\text{O}/^{16}\text{O}$) of the sample and R_{std} = the isotope ratio ($^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$) of the standard.

When water changes state through condensation or vapourisation, isotopic fractionation occurs due to differences in vapour pressures and diffusion velocities in air of the different isotopic species of water (Sidle, 1998, Mazor, 1991). The degree of isotopic fractionation is inversely associated to temperature. There is seasonal variation in the stable isotopic compositions of precipitation at a given location, with more depleted values occurring in the colder months. More depleted values are also observed at higher latitudes.

Precipitation falling at higher elevations is more depleted than that falling at lower elevations; this latter property is of utility in the hydrological applications. Precipitation at

continental locations is more depleted than that which falls nearer the coast (Fritz and Fontes 1980, Clark and Fritz, 1997).

In contrast to the condensation process, evaporation does not take place under equilibrium conditions. The effective fractionation factors are greater than the equilibrium values. When water undergoes evaporation the lighter isotopic species ($^1\text{H}_2\ ^{16}\text{O}$) specially leave the surface, so the remaining water becomes enriched in the heavier isotopic species ($^1\text{H}_2\ ^{18}\text{O}$ or $^1\text{H}_2\text{H}^{18}\text{O}$) (Sidle, 1998, Kendal and McDonnell, 1998, Singh and Kumar, 2005).

The degree of enrichment depends on the temperature, relative humidity of the atmosphere and the hydrological balance of the surface water body. The enrichment of oxygen-18 is about one order of magnitude less than deuterium. An important process which controls the enrichment of the surface water is molecular exchange, which occurs between surface water and the atmospheric water vapour. The deuterium and oxygen-18 values of natural waters obey the following general relation, after Criag (1961):

$$\delta^2\text{H} = a\delta^{18}\text{O} + d$$

For waters which have not been subjected to evaporation the value of 'a' is 8 and the average global value of d for precipitation is 10. The deuterium excess (d), the intercept of the GMWL (Dansgaard, 1964) is defined as:

$$d = \delta^2\text{H} - 8\delta^{18}\text{O}.$$

The ratios of hydrogen and oxygen isotopes are linearly correlated, and the trend of distinctions characterizes the Global Meteoric Water Line (GMWL), where $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$ Craig (1961). Later, Gat and Carmi (1970) suggested for the Mediterranean Meteoric

Water Line (MMWL) the relationship $\delta^2\text{H} = 8\delta^{18}\text{O} + 15$ between $\delta^2\text{H}$ and $\delta^{18}\text{O}$. Akiti (1980) also suggested the Local Meteoric Water Line (LMWL) with the relationship $\delta^2\text{H} = 7.86\delta^{18}\text{O} + 13.61$.

2.7.2 Previous studies of the stable isotopes

Isotopic and hydrochemical compositions, combined with geological and hydrogeological settings, have been used to identify the recharge and flow characteristics and evaluate the continuity of the Lower Cretaceous Nubian sandstone aquifer in the Sinai Peninsula, Egypt. Study results show a considerable depletion in stable isotopic content (^{18}O and ^2H) and low deuterium excess (d-excess) reflecting old meteoric groundwater that recharged the aquifer in pluvial times.

The continuity of the aquifer in the Northern and Central Sinai is evidenced by the isotopic similarity of samples taken from above and below the central Ragarbert El-Naam fault in the area (Samie EL, 2001).

Stable isotope composition of waters established that deep groundwater is an ancient water recharged probably during the late Pleistocene and early Holocene periods in an attempt to understand the mechanism that contribute to groundwater mineralisation in Tunisian Chott's region (Kamel et al., 2008).

Akiti (1986) stated that environmental isotopes have demonstrated to be appreciated in studying the infiltration process and tracing recharge areas. Krabbenhoft et al., (1990) indicated that in areas with narrow water table, stable isotope of water are excellent tracers

of recharge of surface water to groundwater. Guendouz et al., (2003) also stated that, stable isotopes have become a significant tool in the study of geologic processes that affect surface and groundwater and serve as traditional tracers of water source .

In Ghana, groundwater studies using environmental isotopes was initiated in 1980s (Akiti, 1980). Isotopes studies was later focused on source of groundwater (Acheampong and Hess, 2000; Pelig-Ba, 2009), groundwater recharge (Adomako et al., 2010; Fynn et al., 2016), origin of dissolved ions (geogenic and anthropogenic) in groundwater was identified (Gibrilla et al., 2010a; Zakaria et al., 2012), Volta lake and groundwater interaction (Kaka et al., 2011), role of meteoric recharge in the Voltain basin (Yidana, 2013), outlining stable isotopes ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) from meteoric water to groundwater in the Densu River basin of Ghana (Adomako et al., 2015) and estimation of evapotranspiration losses in the vadose zone (Yidana et al., 2016) .

Kaka et al., (2011) used stable isotopes of hydrogen ($\delta^2\text{H}$) and oxygen ($\delta^{18}\text{O}$) in groundwater, streams and Volta Lake in southwestern margin of the Volta Lake to investigate possible intrusion of Volta Lake into aquifers near the banks of the lake.

Account from the study shows that $\delta^{18}\text{O}$ in most of the groundwater (-3.61 to -2.17 ‰ vs VSMOW), depleted in heavy-isotope were in the north-eastern portion of the study area (Kwahu Plateau), and those enrich in heavy-isotopes (from -2.62 to -2.17‰ vs VSMOW) were found in areas in proximity of the Volta Lake. Also, the account from study show that, recharge of groundwater in the area is of meteoric origin with some possible intrusion of Volta Lake into the aquifers near the banks of the Volta Lake. The calculated proportion

of the Volta Lake water in groundwater at Oterkpolu, Bormase Tenya-1, Kasakope, Akrusu-Saisi, Treboanya, and Akotue was reported to be 32 percent, 28 percent, 25 percent, 18 percent, 16 percent and 12 percent respectively. .

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Bongo District

3.1.1 Location and size

The Bongo District lies between longitudes 0.45⁰ W and latitude 10.50⁰ N to 11.09 and has an area of 459.5 square kilometres. It is one of the nine Districts in the Upper East Region and shares boundaries with Burkina Faso to the North, Kassena-Nankana West District to the East, Kassena-Nankana East District to the West and Bolgatanga District to the South . It lies within the Oncho-cerciasis-freed zone.

The district has implications for development due to its location and size, especially in a situation where the district shares borders with Burkina Faso. Thus, amongst others it has the potential of enhancing economic activities between the district and its neighbours in Burkina Faso .

Already in existence is a vibrant market at the Burkina side of the border known as Yelwongo where citizens in the district do brisk business with their neighbours. This trade interaction has brought about increase in household incomes which has a direct influence in the standard of living of the people of both countries. (Dickson and Benneh 1980) .

District is 99.2, the age dependency ratio for males is higher (113.6) than that of females (87.7), (Ghana Statistical Service, 2014) .

3.1.3 Climate

The Bongo District falls under the Tropical continental climatic region. It is characterized by a single rainy season from May to October, followed by prolonged dry season from October to April with hardly any rain. The mean annual rainfall is between 100mm and 115mm. The highest mean annual monthly temperature is about 36 degree Celsius in March and the lowest of about 27 degree Celsius in August. High relative humidities of 70 to 90 percent are record during the rainy season . In the dry season, the lowest value of 20 percent is observed (Dickson and Benneh 1980).

3.1.4 Relief and Drainage

Topography is generally low, gently rolling relief of 90 – 300 meters above sea level.

Exception of these are inselbergs near Bongo (331.0m), which abruptly rise, to heights of 92 – 122m above surrounding lands (District profile, BDA, 2006). The streams and rivers that drain the district, Atankuid-Yaragatanga, river overflow their banks in the main rainy season. The District has one large dam at vea and small dams and dugouts located in Bongo, Zokko, Balungu, Adaboya, Akulmsa, Namoo and Soe-Yindongo (BDA, 2006) .

3.1.5 Geological Setting

The Bongo district is underlain by Birimian metavolcanics and metasediments intruded by Belt and Basin type granitoids. The metavolcanics consist of andesite, basalt, actinolite, schist and tuffs and the metasedimentary also consist of phyllites, quartz-muscovite, quartz-feldspathic, schist and greywacke. The foliation in these rocks are generally easterly, dips between 45 and 65 SE. The rocks are coarse grained porphrogranits generally consisting of hornblende and biotite bearing granitoids and granodiorites with associated quartz veins and doleritedykes. There is also quartz to coarse to medium grained microcline rich granites, foliated and locally referred to as Bongo granites. These intrusives occur within the metasedimentary package and cover most part of the district. The non – hornblende rich granitoids and quartz diorite intrudes the metavolcanic rocks at some place (Murray, 1960, Arhin, 2008) .

3.1.6 Vegetation and Soil Characteristics

The vegetation is guinea savannah woodland consisting of short widely spread deciduous trees and a ground flora of grass, which get burnt by fire or the scorch sun during the long dry season. There is a marked change in the plant life of this vegetation zone during different seasons of the year. In the raining season, the area looks green with life. Tree blossom and grass shoot up rapidly. But soon after the rains, leaves begin to change colour from green to yellow and the trees begin to shed their leaves. The most common economic trees are shear nuts, dawadawa, baobab and acacia . However, regular burning, grazing of livestock and cultivation has resulted in the survival of relatively few trees. The

vegetation in this area is thus, quite open and is dominated by short grasses (Dickson and Benneh, 1980) .

The Bongo group of soils is developed over Bongo granites. They are characterized by numerous groves of baobab trees. The parent materials of the soils have been known to be very productive due to the high potash and phosphate content of the parent rock. Human population densities on these soils are high. Owing to long periods of intensive farming accompanied by mismanagement of the land, soil exhaustion and erosion are prevalent .

Over wide expanses, very severe erosion has resulted in the formation of lithosols. The series of soils are moderately well drained coarse texture soils occupying larger tracts of land on middle and upper slopes and less frequently on summits. Lower slopes soils comprise the Yorogo and Zorko series. The Yorogo series are ground water Laterites consisting of shallow, pale colored and very coarse sands (colluvia) lithosols occurring near valley edges and usually expose partly weathered rock onround surface. Generally, the Bongo soils consist of about 7.62cm of very slightly human-stained, crumbly coarse sandy loan overlying reddish brown, fine blocky, very coarse sandy loan containing occasional incompletely weathered feldspar particles . It grades below into red, mottled pink and yellow coarse sandy clay loan of partially decomposed granite.

The soils are well drained, friable, and porous and possess good filth. Consequently, they have good water holding capacity. They are inherently fertile but for the most part farmed more or less continuously so that they are lacking in organic matter and nitrogen. The soils are rich in phosphate and support crops like millet, sorghum, rice, maize, groundnut,

cowpea, bambara beans and vegetables. However, the high pressure of population and farming activities on the land have rendered the carrying capacity of the soil very low resulting into low soil fertility, low water holding capacity and susceptible to sheet erosion during the rainy .

3.1.7 Groundwater Occurrences

Groundwater is extracted in northern Ghana using hand dug wells, boreholes, and piped systems. Martin and van de Giesen (2005) estimated that the groundwater production in the Volta River basin to be around 88 million m³/yr which is equivalent to less than 5% of the average annual groundwater recharge to the basin. This value suggests that further development of groundwater is possible. Martin and van de Giesen (2005) mentioned that groundwater potential in the region is constrained by availability, accessibility, and economics . The percentage of successful boreholes in the UER (Bongo) is considerably high at 93.8% compared to 60.9% and 90.8% from the northern region and the Upper West region (Carrier, 2008). The drilling success depends mainly on the yield of the well or the quality of groundwater. Groundwater characteristics have been estimated using pump tests from both drawdown and recovery phases of several boreholes in the region .

Unfortunately, the aquifer systems in Ghana are not properly identified yet and there is no single geologic map that delineates the aquifer system [Enoch Asare, Groundwater Division, WRC, written communications]. Similarly, the piezometric elevations are not yet properly monitored and established. It is noticed that the area is characterized by shallow aquifers with low storativity and moderate specific capacity.

In general, groundwater quality in the UER (Bongo) is good but localized groundwater quality problems are present. Some of these concerns include high concentrations of fluoride (Dapaah-Siakwan et al., 2006) .

3.2 Kassena-Nankana West District

3.2.1 Location and Size

The Kassena-Nankana District is located approximately between latitude 10.97° North and longitude 01.10° West. It forms part of the thirteen districts in the Upper East Region of Ghana. Covering a total land area of approximately 1,004 sq. km, it shares boundaries with Burkina Faso to the north, Bongo District to the north-east, Bolgatanga Municipal to east, Kassena Nankana Municipal to the south, Bulsa District south-west and Sissala East District to the west (Ghana Statistical Service, 2014) .

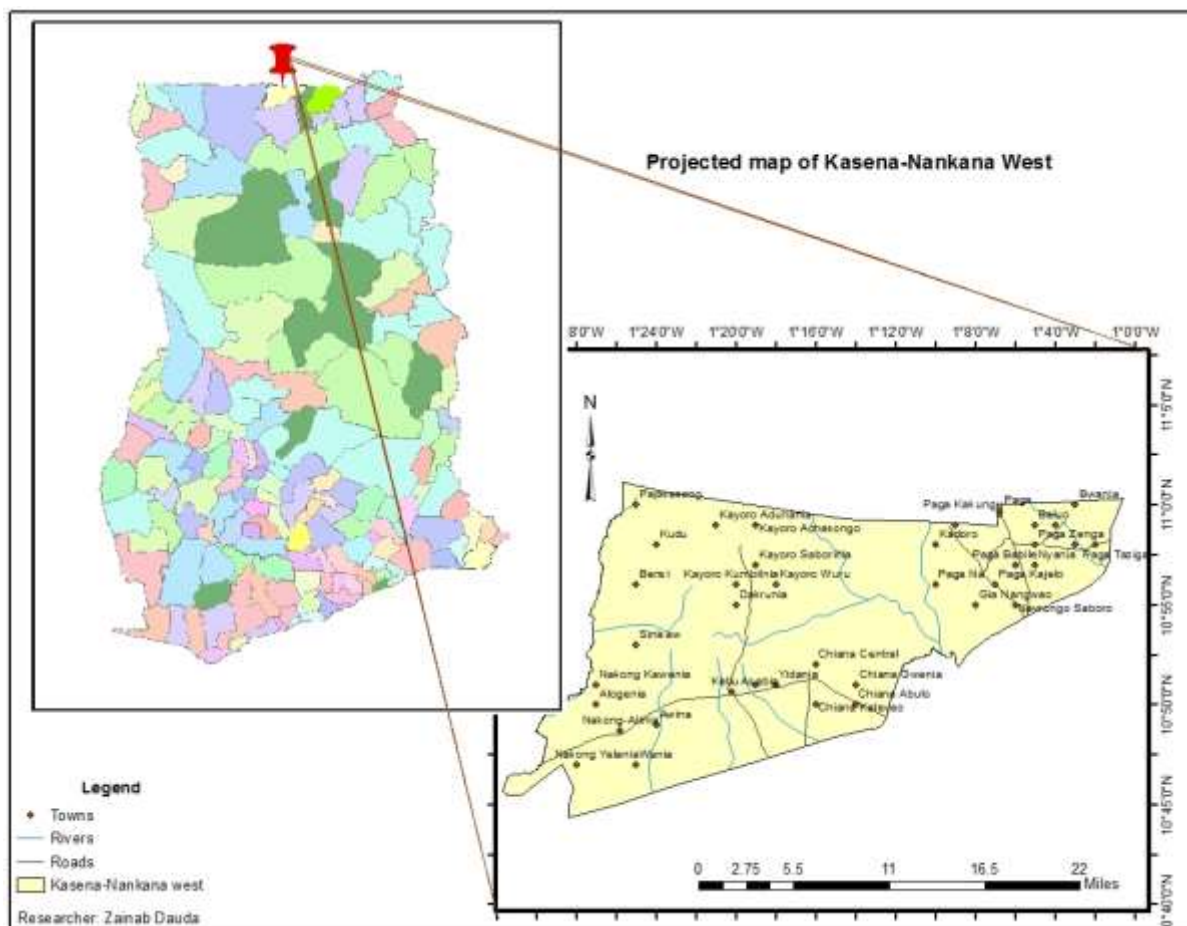


Figure 3.2 Map of Ghana showing Kassena-Nankana West District in Upper East Region

3.2.2 Population Size and Distribution

The district has a total population of 70,667 representing 6.8% of the population of Upper East Region. With an area of 872.8 square kilometres, it has a population density of 81 persons per square kilometre. The proportion of the female population (50.8%) in the area is slightly higher than that of males (49.2 percent). The age category with the highest population is 5-9 years constituting 6.9 percent of the total district population. (Ghana Statistical Service, 2014) .

3.2.3 Relief and Drainage

The district is underlain mainly by Birrimian and Granitic rock formation with a generally low lying and undulating relief with isolated hills rising up to 300 meters above sea level in the western part of the district. Notably among these hills are Fie (9280 metres above sea level), Busono 350 metres, and Zambao 360 metres . The district is mainly drained by the Sissili River and its tributaries. There are, however, some few dug-outs and ponds which are used for livestock rearing, crop production and domestic purposes. (Ghana Statistical Service report, 2013) .

3.2.4 Climate

The Kassena-Nankana West District falls within the interior continental climatic zone of the country characterized by pronounced dry and wet seasons. The two seasons are influenced by two air masses. First is the warm, dusty and dry harmattan air mass which blows in the north easterly direction across the whole district from the Sahara Desert .

During its period of influence (late November – early March) rainfall is entirely absent, vapour pressure is very low (less than 10mb) and relative humidity rarely exceeds 20.0 percent during the day but may rise to 60.0 percent during the nights and early mornings .

Temperatures are usually modest at this time of the year by tropical standards (26-degree Celsius – 28 degree Celsius). May to October is the wet season. During this period, the whole of West African sub-region including Kassena-Nankana West District is under the influence of a deep tropical maritime air mass. This air mass together with rising convection currents provides the district with rains. The total rainfall averages 950 mm per annum. The above- phenomenon adversely affects the water table and reduces underground

water. Water harvesting is probably a viable option in the district. (Ghana Statistical Service, 2013) .

3.2.5 Geological Setting

Kassena-Nankana West District is generally underlain by the West African Craton comprising of the Birimian (e.g Kesse 1985; Luebe et al., 1990; Taylor et al., 1992) just like the adjoining communities falling within the Bole-Nangodi belt. The Birimian here is generally intruded by two suites of granitoids, all trending in a NE-SW direction. The Bongo type granitoids can generally be classified as granites consisting of hornblende and or biotite and muscovite-bearing, with apatite, epidote and sphene occurring as accessory minerals (Abitty et al., 2016) . The Birimian volcano-Plutonic, synvolcanic intrusive - biotite granitoid; undifferentiated mostly granodioritic rocks covers most parts of the study area. These granitoids have intruded the Tarkwaian sedimentary rocks which overlie the Bole-Nangodi belt (Taylor et al., 1992) .

These basement rocks are key to the development of aquifers in the area. Over the last decade there has been an increase in the number of boreholes drilled in the area, though groundwater recharge in the area is limited due to high evapotranspiration (Smedley et al., 2002). Average recharge is estimated at about 4 percent of annual rainfall, or about 40 mm a⁻¹ (Apambire et al., 1997). Some workers have also reported the capping of some boreholes in due to high fluoride concentrations above WHO threshold of 1.5 mg/l. Though the study area is drained by some rivers and there are other sources of water, a study by the

Ghana Statistical Service showed about 72.7percent households obtain their drinking water from boreholes .

3.2.6 Vegetation and Soil

The vegetation is mainly of Sahel Savannah type consisting of open savannah with fire swept grassland separating deciduous trees among which may be seen a few broad-leafed and fire-leached tree species. Some of the most densely vegetated parts of this district can be found along river basins and forest reserves. Examples are the Sissili and Asibelika basins. Most of these trees in the forested areas shed their leaves during the dry season. The human activities over the years have also affected the original vegetation considerably. Common trees which are also of economic importance include Dawadawa, Sheanut, Baobab, Nim and Mango. The low vegetation cover of the area hampers sufficient rainfall thereby reducing underground water supply.

Two main soil types can be found in the district. These soil types are the Savannah Ochrosols and the Groundwater Laterites. The northern and eastern parts of the district are covered by the Savannah Ochrosols, while the rest of the district is characterized by ground water laterite. The Savannah Ochrosols are porous, well drained, loamy, mild acidity and interspersed with patches of black or dark grey clay soils. This soil type is suitable for cultivation of cereals and legumes. The groundwater laterites are developed over shale and granite. Due to the underlying rock type, they become water logged during the rainy season and dry up during the dry season, thus causing cemented layers of iron-stone which make

cultivation difficult. This would probably have contributed significantly to food insecurity in the district (Ghana Statistical Service, 2014).

3.3 Data Collection

Prior to sample collection, data related to the study to be undertaken in the study area was reviewed through a Desk Study. A Field Reconnaissance Study was also undertaken to get first-hand information on key activities in the area related to the study.

3.3.1 Desk Study

Literature review, collection of topographical maps, collection of data from Ghana Meteorological Agency and the Geological Survey Department (GSD) in Bongo and Kassena Nankana West was carried out to assess the general hydrological and hydrochemical facies of groundwater. Equipment required for measurement of important physico-chemical parameters on the field was also assessed .

3.3.2 Reconnaissance Field Work

Two months Reconnaissance field survey was carried out to identify the sampling points, the type of kits that were needed for the sampling task, and groundwater to be collected.

3.4 Field Work

3.4.1 Sample Collection

Total of sixty-four (64) boreholes points were sampled. The locations of the sampling points are shown in fig (3.3). Groundwater samples were collected from active water supply wells used for domestic purposes. To obtain homogeneous samples and fresh aquifer samples for analysis, aquifers of stagnant water were purged for 30 minutes. The Samples were first collected in a sterilized bucket, filtered through 0.45 μ m cellulose filter using a hand-operated vacuum pump. The filtered samples were quickly transferred into 250 mL pre-conditioned high-density polyethylene bottles after washing with 5% nitric acid, and then rinsed several times with distilled water for the cation's samples and capped. This was carried out to ensure that the sampling bottles were free from contaminants.

The Samples for the isotope's analysis were not filtered. The 100 mL bottles from a secondary polyethylene container were directly filled with water to the brim to avoid air bubbles and then was tightly sealed, (IAEA, 2010).

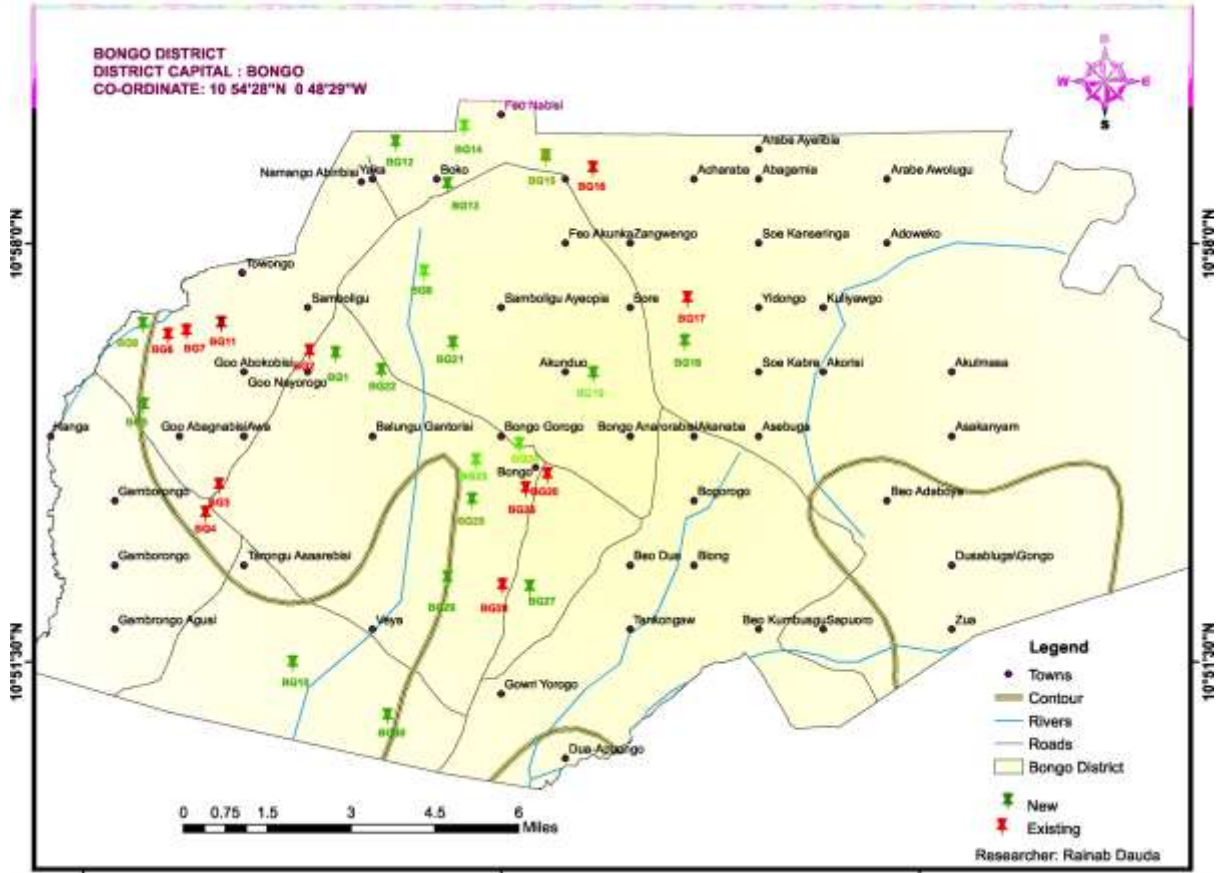


Figure 3.3 A Map showing the sampling point of Bongo District

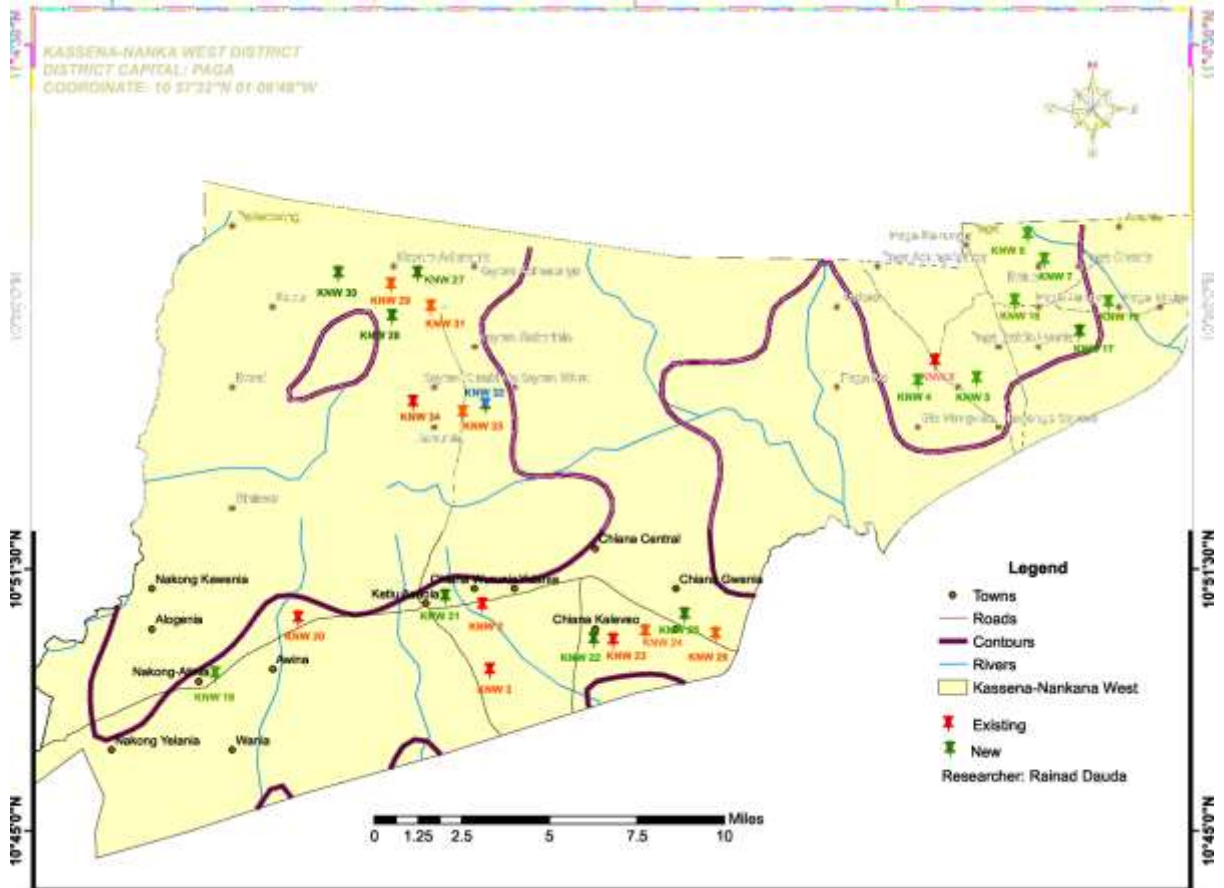


Figure 3.4 A Map showing the sampling points of Kassena-Nankana West District

3.4.2 Field Measurements

On-site determination of Temperature, electrical conductivity (EC) and total dissolved solids (TDS) were conducted in the field by the HACH conductivity and pH metre. The measurement of these variables in situ was necessary since these parameters are likely to change during transport. The samples were kept in the refrigerator until laboratory analyses were carried out.

3.4.2.1 pH

The HACH pH meter was calibrated using buffer solutions of pH 4.01 and 7.00 and the probe was dipped into water sample collected in sample bottle and covered with clear-wrap. This was done to minimize the degree of alteration that might occur once the sample is obtained from the aquifer, physical controls guiding the H⁺ activities alter and leads to alterations in pH (Trevor, 1990). Digital readout was taken when readout was uniform.

3.4.2.2 Total Dissolved Solid, Salinity, Electrical conductivity (EC), and Temperature

Total Dissolved Solid, Salinity, Electrical conductivity (EC), and Temperature of water samples were obtained using the Hanna HI 991301 multi-functional conductivity meter. Three standard Potassium Chloride solutions of conductivities 84 $\mu\text{S}/\text{cm}$, 1814 $\mu\text{S}/\text{cm}$ and 5000 $\mu\text{S}/\text{cm}$ was used to calibrate the meter. The electrode was cleansed in distilled water accompanied by sampled water. The electrode was dipped into the sample and was gradually moved circularly for a minute until digital readout was attained.

3.4.2.3 Bicarbonate (HCO_3^-) Alkalinity

Alkalinity and bicarbonate contents of the water samples were determined by titrimetric using HCl as titrant and methyl orange indicator. Alkalinity is a measure of ability of water to neutralize acids. The contents of HCO_3^- , CO_3^{2-} were assessed together by titration against standard acid (HCl) using methyl orange as indicator in the resolve of total alkalinity. Transferred of about 25mL aliquot of the water sample was made into a 125mL conical flask. Two drops of methyl orange indicator were added. To mix thoroughly, the contents of the conical flask were swirled (a yellow colour was developed).

The water sample was then titrated against 0.02M HCl solution, till the yellow colour change to orange (signifying the end of the titration). The volume of titrant (HCl) used was recorded. Consistent titres were obtained and were averaged. Hence, the concentration of HCO_3^- in mg/L was evaluated from the equation below;

$$[\text{HCO}_3^-] = \frac{V_{\text{HCl}} \times C_{\text{HCl}} \times M_{\text{HCO}_3^-}}{A} \quad (3.1)$$

where,

V_{HCl} is the volume of HCl used (average titre volume),

C_{HCl} is the molarity of HCl, A is the volume of water (aliquot) in L, and $M_{\text{HCO}_3^-}$ is molar mass of HCO_3^- (Drever,1982a; Hill,2000; Trever,1990).

3.5 Laboratory Analysis

The samples were analysed at the Nuclear Chemistry and Environmental Research Centre, Ghana Atomic Energy Commission. HCO_3^- titration was done at the wellhead using a HACH digital Titrator. Na^+ and K^+ were analysed using flame photometer (Sherwood model 420), Mg^{2+} and Ca^{2+} using Varian AA240 Fast Sequential Atomic Absorption Spectrometer. F^- , PO_4^{3-} , Cl^- , SO_4^{2-} and NO_3^- were analysed using ICS-90 ion chromatography.

3.5.1 Major ions Analysis

3.5.1.1 Sodium and Potassium (Na^+ and K^+)

Sodium and Potassium (Na^+ and K^+) levels in the samples were determined using Sherwood Model 420 Flame photometer. The instrument has the following components; the burner, nebulizer and mixing chamber, simple colour filters (interference type) and photo-detector.

Three (3) standards (20, 50 and 100 mg/L) Na^+ and K^+ mixture was prepared by diluting 2, 5 and 10 mL each of stock solution (equal volume mixture of Na^+ and K^+) with distilled water into 100 mL solutions. The instrument was first zeroed by aspirating a thoroughly mixed 2 mL of 100 mg/L Li solution and 5 mL distilled water. The instrument was then calibrated using the three (3) standards (mixed Na and K calibration standards) by aspirating thoroughly mixed solution of 2 mL 100 mg/L Li solution and 5 mL of the mixed standards of Na and K.

After calibration, water samples were prepared for analysis by pipetting 2 mL of 100 mg/L lithium solution to every 5 mL of water sample in test tubes and thoroughly mixed by swirling. This was done to minimize interference. The concentration of Na^+ or K^+ , $C(\text{Na}^+$ or $\text{K}^+)$ in mg/L in water samples were calculated using equation (3.2):

$$C(\text{Na}^+ \text{ or } \text{K}^+) \text{ in mg/L} = C(\text{Na}^+ \text{ or } \text{K}^+) \text{ FP in mg/L} \times D_f \quad (3.2)$$

where,

D_f is the dilution factor, $C(\text{Na}^+ \text{ or } \text{K}^+) \text{ FP in mg/L}$ is concentration read from flame photometer

3.5.1.2 Magnesium (Mg^{2+})

Magnesium (Mg^{2+}) levels in water samples were determined using VARIAN AA 240 Fast Sequential (FS) Atomic Absorption Spectrometer equipped with a deuterium background corrector.

Sub-stock solution (10 mg/L) was set by diluting 1 mL of stock solution (1000 mg/L Mg) with distilled water into 100 mL solution. The instrument was calibrated using three working standards (0.1, 0.2 and 0.5 mg/L) by diluting 1, 2, and 5 mL each of the sub-stock solution with distilled water into 100 mL solution.

After calibration, samples for analysis were organised by carefully mixing 1 mL of the water sample with 9 mL of 100 mg/L Lanthanum solution in a test tube. Samples were then articulated into the atomic absorption spectrometer (AAS) and for every 10 readings a standard is aspirated as a quality control measure.

The concentration of Mg^{2+} , $C_{(Mg^{2+})}$ in mg/L in water samples were calculated using the equation below .

$$C_{(Mg^{2+})} \text{ in mg/L} = C_{(Mg^{2+}) \text{ AAS in mg/L}} \times D_f \quad (3.3).$$

where,

D_f is dilution ratio of factor, $C_{(Mg^{2+}) \text{ AAS}}$ is concentration Mg^{2+} read from the AAS.

3.5.1.3 Calcium (Ca^{2+})

Ca^{2+} ions in water samples were evaluated using complexometric titration (EDTA method) at the Inorganic Chemistry Laboratory.

Twenty-five millilitres (25 mL) of water sample was pipetted into a conical flask, 2.0 mL NaOH solution was added, and stir for basic conditions (pH 12 to 13) to be achieved. About 0.1 g of murexide indicator was then added to the mixture. With constant twirling, the EDTA (ethylenediaminetetraacetic acid or its salts) titrant was then titrated against the water samples to attain proper end point.

A metal ion reacts with an accurate ligand to form a compound and homogeny point of the titration is evaluated by an indicator in complexometric titration. The EDTA in water containing calcium can form compound, and in the presence Murexide (ammonium purpurate) indicator changes from pink to purple indicating end of the reaction, when all the calcium has been complexed by the EDTA at a pH of 12 to 13. The volume of EDTA used to reach end was read as titre and the procedure was repeated for three times to obtain consistent titre and averaged.

The Ca^{2+} and EDTA reaction equation is as follows ;



where,

Y^{4-} represent the EDTA ion at basic conditions.

Concentration of Ca^{2+} ion in mg/L was calculated as follows:

$$[\text{Ca}^{2+}] = \frac{V_{\text{EDTA}} \times C_{\text{EDTA}} \times M_{\text{Ca}^{2+}}}{V_{\text{sample}}} \quad (3.5).$$

where,

V_{EDTA} is “volume of titre in mL, C_{EDTA} is concentration of EDTA solution mol/L, $M_{\text{Ca}^{2+}}$ is molar mass of Ca^{2+} , and V_{sample} is volume of water sample used in L.

3.5.1.4 Major and Minor Anions (F^- , Cl^- , NO_2^- , PO_4^{3-} , and SO_4^{2-})

The Levels of anions (F^- , Cl^- , NO_3^- , PO_4^{3-} , and SO_4^{2-}) were determined using Dionex ICS-90 Ion Chromatograph (IC) at Inorganic Chemistry Laboratory, GAEC, Kwabenya, Accra. The IC performs isocratic ion analyses using suppressed conductivity detection. The instrument has a liquid eluent, a high-pressure pump, a sample injector, a separator column, a chemical suppressor, and a conductivity cell.

The procedure of ion chromatography involves injecting water sample into a stream of carbonate-bicarbonate eluent, which passes through a series of ion exchangers. The anions of interest are separated based on their relative affinities for a low capacity, strongly basic anion exchanger (guard and separator columns). The separated anions are directed through a micromembrane suppressor which is cleansed with a continuously flowing strong acid solution (regenerant solution). In the suppressor the separated anions are converted to their highly conductive acid forms and the carbonate-bicarbonate eluent is converted to weakly conductive carbonic acid. The separated anions in their acid forms are measured by conductivity. They are identified based on retention time as compared to that of standards. Quantitation is by measurement of peak area or peak height.

Three (3) standards were prepared by diluting each 10, 20 and 30 mL of stock solution [Dionex seven anion standard (II)] with deionized water into 100 mL solution.

Using a prewashed syringe of 1 mL capacity, standards were injected to calibrate the IC. The water samples were then injected. Acquisition and quantification of the chromatographic spectrum was achieved using the DIONEX CHROMELEON Chromatographic Data Management System Software (Thermo Scientific, USA).

3.5.2 Trace metals parameters (As and Fe)

3.5.2.1 Samples Digestion

4.5 mL of conc. HCl and 0.5 mL conc. HNO₃ into 40 mL of water samples were pipetted into a 100 mL borax glass beaker and placed on a hot plate for 3 hours in a fume hood. A volume of 30 mL (nominal volume) was prepared after the digested samples were made to cool, filtered and diluted with double distilled water.

3.5.2.2 As Analysis

Dilution of 1 mL of stock solution with distilled water into 100 mL solution was used to prepared 10ML sub-stock solution. The instrument was calibrated with standards (0.2, 0.4, 0.6, 0.8 and 1.0 mg/L) which were made by diluting 2, 4, 6, 8 and 10 mL of sub-stock solution with distilled water into 100 mL solution. Samples were then transferred into the Atomic Absorption Spectrometer (AAS) and a standard was added to every 10 readings as a quality control measure.

The concentration of As in each water sample read from the AAS was used to compute for the As final concentration of the water samples from equation.

$$\text{Final conc. (mg/L)} = \frac{\text{Conc.}_{\text{AAS}} \times D_f \times \text{Normal volume}}{\text{Sample volume (mL)}} \quad (3.6)$$

Where,

D_f is dilution factor, and $\text{Conc.}_{\text{AAS}}$ is concentration of As read from the AAS (AAW, 1999).

3.5.2.3 Fe and Mn using FAAS

The stock solution of 10.0mL Fe and Mn were diluted with distilled water into 100mL solutions to prepared sub -stock solution of 100.0mg/L

Dilution of Fe and Mn sub-stock solution with distilled water into 100 mL solutions were used to prepare three (3) working standards 2,5,10 mg/L Cd which was used to calibrate the instrument.

For every 10 readings, a standard was aspirated after the digested samples were aspirated into the Atomic Absorption Spectrometer (AAS). The final concentration of FE and Mn in the water sample is given by equation

$$\text{Final conc. (mg/L)} = \frac{\text{Conc.}_{\text{AAS}} \times D_f \times \text{Normal volume}}{\text{Sample volume (mL)}} \quad (3.7)$$

where,

D_f is dilution factor, and $Conc._{AAS}$ is concentration of Fe read from the AAS.

3.5.3 Stable Isotopes Analyses (δ^2H and $\delta^{18}O$)

Oxygen-18 and deuterium in all the samples were analysed using the Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) Los Gatos Research DT-100 Liquid–Water Isotope Analyser (Model 908-008-2000) at the Isotope Hydrology Laboratory of the Nuclear Chemistry and Environmental Research Centre, Ghana Atomic Energy Commission. All stable isotope data are reported in the usual δ notation, where

$$\delta = \left[\frac{R_{sample}}{R_{vsmow}} - 1 \right] \times 1000 \quad (3.8)$$

R represents either the $^{18}O/^{16}O$ or D/H ratio of the sample, and R_{vsmow} is the isotope ratio of the V-SMOW, a reference standard .

1mL aliquot of dummy samples, water samples and standards were pipetted into 1.5ml labelled autosampler glass vials with 1ml automatic pipette with disposable tips and were then closed with PTFE septum caps. The dummy sample, the heavy isotope calibration standard; the light isotope calibration standard; the third standard (the control standard); and five water samples followed by three standards were placed in their proper positions on the autosampler tray respectively.

After 25minutes of samples analysis, the outcomes were then assigned onto a memory stick for archiving and post-processing and the IAEA spreadsheet was used for post-processing of the outcomes.

The stable isotope composition of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were estimated comparative to internal standards that were calibrated using the Vienna-Standard Mean Ocean Water (VSMOW) (Coplen, 1996). Post-processing procedure was used to compute delta-scale values with respect to the Vienna Standard Mean Ocean Water (VSMOW) by the equation below

$$\delta = \frac{R_{\text{measured}} - R_{\text{vsmw}}}{R_{\text{vsmw}}} \quad (3.9)$$

where R is $^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$.

3.6 Quality Assurance/Quality Control (QA/QC) Measures

Quality assurance (QA) is the policies, procedures and actions established to provide and maintain a degree of confidence in data integrity and accuracy (Sundaram et al., 2009).

Quality control (QC) is a sample or procedure intended to verify performance characteristics of a system (Sundaram et al., 2009) .

The following sets of operating principles were adopted to help produce data that is of known, consistent and defensible quality.

- (i) To ensure that the sample bottles were free from contamination, which could affect the concentrations of various ions in the water samples, all glassware and sampling containers were soaked in nitric acid (10 % HNO_3) for three (3) days and rinsed with deionized water before use
- (ii) Boreholes were purged for ten minutes to flush the stagnant water retained in pipes.
- (iv) An identification labels were provided on the water samples collected on which the following information were written,

a. Sample identification number.

b. Date and time of sampling.

c. Record of any stability treatment.

d. Prevailing weather conditions at the time of sampling.

(v) Additional samples (apart from the three replicates) were collected at some sampling points to check analytical precision of sampling and analysis.

(vi) Samples that require preservation and special treatment for transportation to prevent their deterioration were treated promptly.

(vii) Reagents used during analysis were of all analytical grades.

(viii) Every instrument used was calibrated with standard chemical solutions prepared from commercially available chemicals and validated with Standard Reference Materials (SRM) and Certified Reference Materials (CRM). The SRM were analysed repeatedly at predetermined intervals to confirm that the method remained in a state of statistical control.

(ix) The accuracy of the laboratory analysis was checked by looking at the anion-cation balance and only those results within ± 5 percent were relied on for subsequent interpretation.

3.7 Determination of Charged-Balance Error (CBE) of the Samples

The accuracy of the analyses was estimated from the charge balance error (CBE) (Freeze and Cherry 1979) using the equation below. The results were within $\pm 5\%$ for most of the samples and few samples were within $\pm 5-10\%$.

Charge balance error (E)

$$E = \frac{\sum zmc - \sum zma}{\sum zmc + \sum zma} \times 100 \quad (3.10)$$

Where, E is the charge balance error, z is the ionic valence, m_c is the molarity of the cation species and m_a is the molarity of the anion species .

3.8 Methods Used in Geochemical Data Analysis

3.8.1 Graphing Techniques

The interpretation of groundwater chemistry can be done using graphical presentations like piper diagrams, Gibbs plots, stiff patterns and diagrams, flow path observation or molar relationships. Graphical Procedures form one of the predictable methodologies used in presenting chemical data of major ions that typifies groundwater.

The bivariate, Gibbs and Piper plots help provide a better understanding of the groundwater chemistry, weathering processes and geochemical evolution (Adomako, 2010).

The Piper trilinear diagram is another graphical and generally used technique important for reduction of chemical data. It was developed by Piper (1944) and consists of two equilateral triangles adjacent each other and a diamond-shaped quadrilateral between the two triangles. One of the triangles represents the concentration of major cations. The other triangle represents the major anions. Piper diagrams are more robust due to its ability to handle more data points.

The Piper Diagram serves as the basis for the classification of water types (Back, 1966).

In general, Piper (groundwater chemical evolution model) reveals groundwater hydrochemical facies in any catchment (Appelo and Postma, 1996a; Edmunds et al., 2002, 2003; Freeze and Cherry, 1979). Piper plots help provide a well-known groundwater, weathering processes and geochemical evolution chemistry (Adomako, 2010). The major advantages of the Piper plot are that it can be used to identify mixing of waters (Appelo and Postma, 1996c) and major analysis can be plotted on the same diagram (Adomako, 2010).

The Gibbs (1970) diagram plots the total dissolved solids (TDS) on a logarithmic axis against the ratio of sodium and the sum of sodium and calcium on a linear axis. It is used to describe some of the mechanisms that govern the chemical structure of inland waters.

Clusters that plotted within the “evaporation-crystallization dominance” field on grounds of high TDS and high $\text{Na}/\text{Ca} + \text{Na}$ ratio were apparently due to elevated TDS and sodium concentration arising from saline seawater intrusion.

Yidana (2008) and Yidana et al. (2010) reported that rock dissolution is a main process deploying groundwater hydrochemistry in the major hydrogeological topographies of Ghana. The concentrations of the major physico-chemical parameters are relatively low where silicate mineral weathering is the major governing process.

Mahlknecht et al., (2004) however noted that even though graphical representations are very helpful in the preliminary evaluation of ground water types and of the relationships between ground water and lithology, the graphical display has the following setback;

The graphical display deals with limited number of chemical elements and therefore seems in the explanation as one would have to choose which component to represent (Guler et al., 2002). Despite this disadvantage of the graphical technique, graphical technique remains a preferable technique for investigating ground water chemistry for many.

In this study the graphing software used for the bivariate plot, Gibbs and Piper diagram were Microsoft Excel software (Office 2013), SPSS software and Diagrammes software [Roland SIMLER Laboratoire d'Hydrogéologie d'Avignon (version 6.5)], respectively.

3.8.2 Multivariate Statistical Analysis

Multivariate statistical analysis was used to determine the distinctions, relations, circulations of the hydrogeochemical data along the study. Some of the multivariate techniques include Cluster Analysis (CA), Principal Component Analysis (PCA) and Factor Analysis (FA). These are effective methods of using, understanding and representing data concerning groundwater chemistry and contaminants (Belkhiri et al., 2010).

It is commonly referred to a range of statistical techniques and methods which mainly comprises data with numerous variables, with the objective of studying the dependence relations between the involved variables (Hamdan, 2012).

Multivariate statistical method has also been employed to recognise the different sources of solutes in groundwater

- (a) contamination from agricultural and urban wastewaters,
- (b) dissolution of calcium and magnesium carbonate minerals,
- (c) evaporative effects due to intensive irrigation,
- (d) weathering of acid volcanic minerals,
- (e) leaching of halite deposits of meteoric origin and
- (f) alteration of manganese containing alkaline silicates (Mahlknecht et al., 2004).

Cloutier et al. (2008) applied two multivariate statistical approaches, principal components analysis (PCA) and hierarchical cluster analysis (HCA) to a subgroup of a dataset made up of 144 samples and 14 parameters to detect geochemical processes controlling groundwater geochemistry and to estimate their practicality to categorize the groundwater samples. The following factors were recognized as manipulating the evolution of groundwater:

- (a) the geological history of the area
- (b) hydrogeological characteristics represented by the level of confinement and the hydraulic gradient; and
- (c) geological characteristics including sedimentary rock type and till mineralogy

Pelig-Ba (1998) used descriptive statistical methods to explain that groundwater from some crystalline rocks in the Upper East Region indicate higher trace element concentrations as compared to their concentrations found in natural water systems.

Finanko et al., (2010) used the technique to display that ground water in his studied area is fresh and usually fit for resources.

Agglomerative Hierarchical Clustering (AHC) is a method of cluster analysis that group together the most similar hydrochemical data and then the groups of hydrochemical data into a hierarchy tree (Husson, Lê, and Pagès, 2011a). The Ward method (Ward, 1963) for agglomerative hierarchical clustering applies clustering in such a way that the fusion of two clusters is determined by the size of the incremental sum of squares. In this study, descriptive statistical methods and the Ward method was employed using SPSS software (SPSS, Ver16.0) 2001.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

This chapter deals with the interpretation of groundwater chemistry, stable isotope ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) content in the two (2) study areas. Additionally, all the data obtained from the studies will be discussed.

4.1 Bongo District

4.1.1 Physio-Chemical Parameters

4.1.1.1 The PH

The pH values of the groundwater samples ranged from 6.06 to 7.17 with a mean value of 6.69. This may imply that the groundwater in the area display moderately acidic to moderately alkaline in nature. The nearly neutral to slightly alkaline was reported in earlier works done in the study areas, (Akiti, 1980, 1982; Martin, 2006; Pelig-Ba, 1998). However, most of the samples analyzed have pH values within the WHO (2004) recommended limit for portable water, ie 6.5 to 8.5.

4.1.1.2 Total Dissolved Solids (TDS) and Electrical Conductivity (EC)

The TDS of the samples are in the range of 63 mg/L and 339 mg/L with mean value of 271.24 mg/L and the electrical conductivity (EC) value range from 115.4 $\mu\text{S}/\text{cm}$ to 708 $\mu\text{S}/\text{cm}$ with mean value of 373.76 $\mu\text{S}/\text{cm}$. Generally, low TDS and EC values are as a result of short residence time of the groundwater or slow disintegration of granitic rock in the study areas as suggested by (Kortasi ,2004). This means that almost all the groundwater

from the areas are fresh water since the TDS values of the study areas are less than 1,000 mg/l (Davis and Wiest, 1996).

4.1.1.3 Temperature

The groundwater temperature variation in the study area range from 31.1 °C to 33.5 °C and the groundwater samples in area are mostly colourless. The differences in temperature can be due to numerous features such as well depth and the flow, different sampling time and the season (Chapman and Kimstah, 1996).

4.1.2 Hydrochemistry of Groundwater.

The basic chemistry of groundwater samples with respect to presence of some vital cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (SO_4^{2-} , HCO_3^- and Cl^-) were used to investigate the processes accounting for the levels in groundwater in this study. The release of ions into groundwater generally depends on temperature, the relative solubilities, rate of supply of H^+ and reaction kinetics of the minerals, (Adomako, 2010). The solubility of the minerals is naturally determined by the act of carbon dioxide (Appelo and Postma, 1996b; Drever, 1982b).

A statistical summary of hydro-chemical groundwater parameters in Bongo District is presented in Table 4.1.

Table:4.1 Descriptive Statistical summary of hydrochemical parameters of Bongo

| Parameter | Minimum | Maximum | Mean | WHO 2004 | MPL |
|-------------------------------|---------|---------|--------|-------------|-----|
| E _c | 115.40 | 708.00 | 373.76 | | |
| pH | 6.06 | 7.17 | 6.79 | 6.5-8.5 | |
| TDS | 63 | 389 | 205.53 | - | |
| Temp | 30.70 | 33.50 | 32.10 | | |
| HCO ₃ ⁻ | 24.00 | 132.0 | 64.96 | 380 | |
| Ca | 6.40 | 60.00 | 24.44 | 200 | |
| Mg | 0.59 | 1.33 | 1.11 | 150 | |
| Na | 12.60 | 86.80 | 48.44 | 200 | |
| K | 0.50 | 8.71 | 3.73 | 30 | |
| F ⁻ | 0.29 | 3.74 | 1.39 | 1.5 | |
| Cl ⁻ | 22.01 | 169.54 | 81.28 | 250 | |
| NO ₃ ⁻ | 0.33 | 12.25 | 5.46 | 10 | |
| PO ₄ ³⁻ | 0.01 | 1.10 | 0.28 | - | |
| SO ₄ ²⁻ | 0.01 | 11.00 | 3.79 | 400 | |

4.1.2.1 Major and Minor ions

Na^+ is the most dominant cation in the major cations' concentrations in Bongo. The order of abundance of the cations is $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$. The higher concentration of K^+ more than Mg^{2+} may be due to the use of potassium fertilizer from agriculture.

The concentration of Na^+ in the study area ranges from 12.60 mg/l to 86.80 mg/l, with a mean value of 48.44 mg/l. All the Na^+ samples are less than the (WHO, 2004) permissible limit of drinking water standard.

The Ca^+ concentration ranges from 6.40 mg/l to 60 mg/l with mean value of 24.44 mg/l which is within the permissible limit of drinking water, per WHO (2004) drinking water standard.

Mg^{2+} and K^+ are within the desirable limit with mean values of 1.11mg/l and 3.73mg/l respectively.

Also, the relative abundance of the anions in Bongo District is Cl^- , HCO_3^- , NO_3^- and SO_4^{4-} , respectively, with Cl^- been the most dominant anion. The concentration of Cl^- in the study area ranges from 22.01 mg/l, to 169.59 mg/l, with a mean value of 81.28mg/l. The higher concentration of Cl in the study area are as a result of leaching from irrigation discharge, animal feeds, surface run-off from inorganic fertilizers resulting from agricultural fields.

All the Cl^- samples are less than the WHO (2004) permissible limit of drinking water standard.

The HCO_3^- concentration ranges from 24.0 mg/l, to 132 mg/l with a mean value of 64.91 mg/l and is within the permissible limit of drinking water standard WHO (2004).

The level of NO_3^- varies from 0.33 mg/l to 12.25 mg/l, with a mean value of 5.46 mg/l. Most of the samples are within the desirable limit of drinking water, except two boreholes BG4 at Tarongo and BG 8 at Aberingabiisi where the concentrations of NO_3^- are 12.25 mg/l and 10.16 mg/l which is above drinking water standard WHO (2003). The higher concentration of NO_3^- in these areas is suspected be as a result of leachate from open defecation, animals drop and septic tanks.

The level of SO_4^- is within the desirable limit of drinking water standard with mean values of 3.79 mg/l and ranges from 0.01 mg/l to 11.00 mg/l.

Fluoride concentrations exhibited a wide variation ranging from 0.29 mg/L to 3.74 mg/L, with an average value of 1.39 mg/ L. The highest values were detected in Aberingabisi CHPS Compound (3.74 mg/ L), Sambolo Basic School (3.46 mg/L), Atampiisi CHPS Compound (2.34 mg/L), Bongo Senior High School (2.62 mg/ L) ,St. Ann Primary School (2.76mg/ L), Aberingabisi (1.97mg/ L), Anafobisi Zuen (1.96 mg/ L) and St. Ann Primary School (1.98 mg/ L). This represents about 53 percent of the sampled groundwater and rest are within the desirable limit of drinking water standard WHO (2004).

High F^- are associated with high Cl^- , HCO_3^- , Na^+ and low concentration of Ca^{2+} as suggested by Li et al (2018) and Wu et al., (2015). The geochemical characteristics F^- in groundwater in the study area is mainly govern by the interplay of Na^+ release and Ca^{2+} removal .

PO_4^{3-} is within the desirable limit of drinking water standard WHO (2004) with mean values of 0.28 mg/l

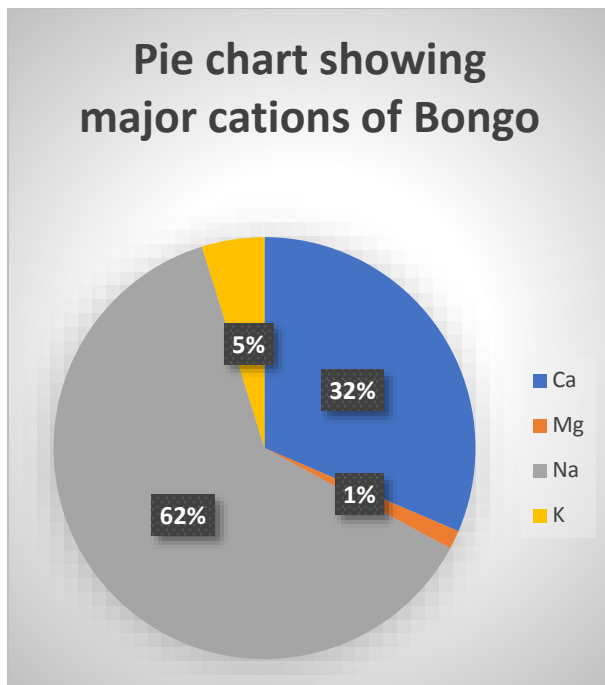


Figure 4.1 Major cations in Bongo District

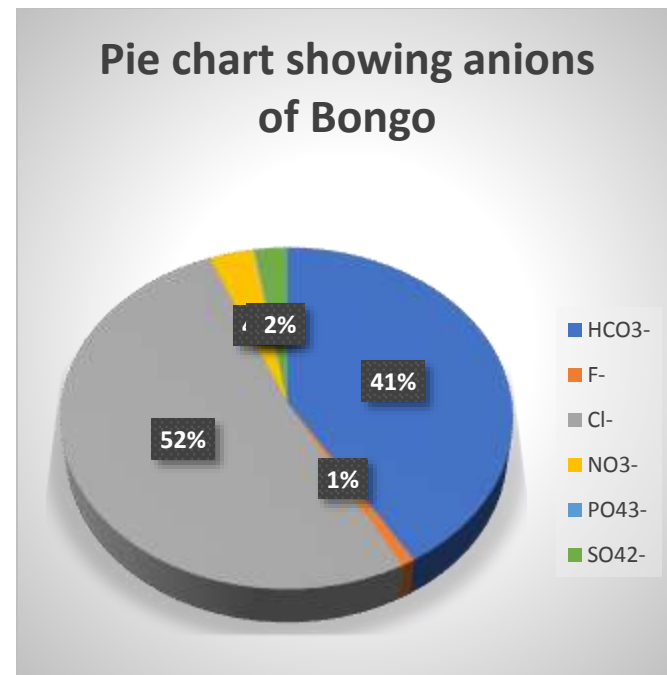


Figure 4.2 Major anions in Bongo District

4.1.3 Mineralisation Process

To identify the origin and the processes of groundwater mineralization, bivariate plots were used to investigate the compositional relations among the dissolved ions. An examination was made by the stoichiometric relation of the major ions Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- observed in groundwater in the study area. The plot of the sum of cations (Σ cations) versus Na^+ and Ca^{2+} , respectively.

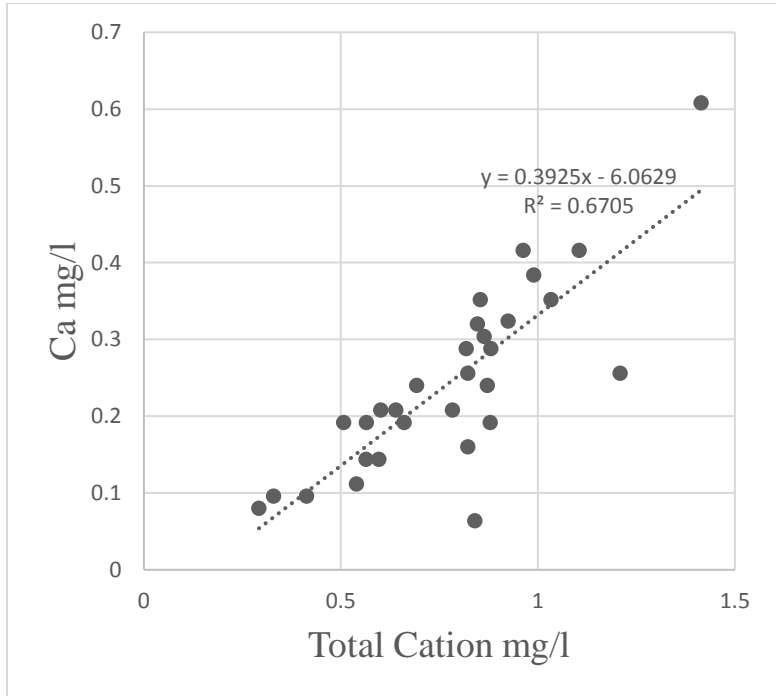


Figure 4.3 Plot of Ca mg/l versus Total Cation mg/l

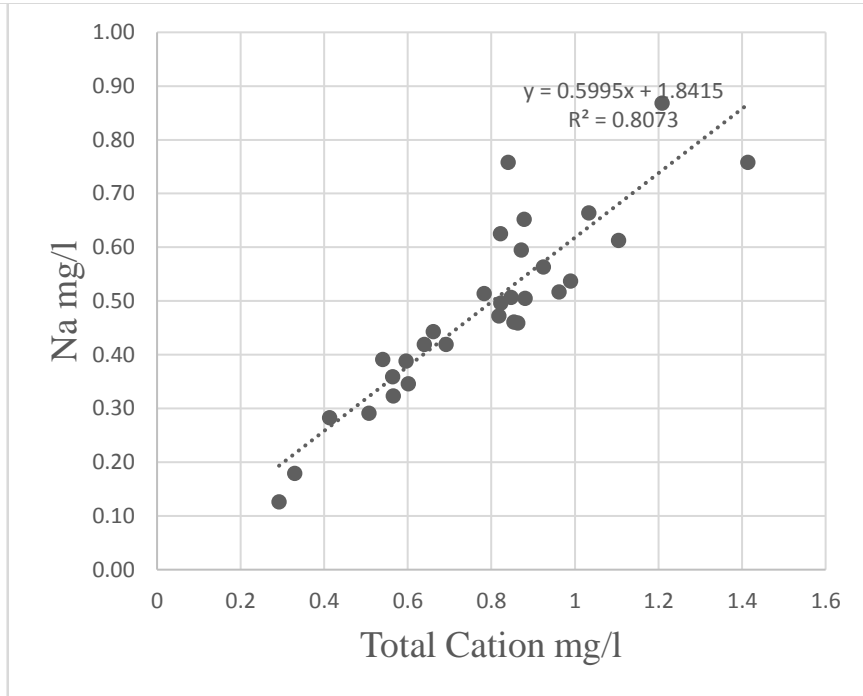


Figure 4.4 Plot of Na mg/l versus Total Cation mg/l

A plot of Na^+ (mg/L) against total cations (mg/L) from (fig 4.4) showed strong correlation implying sodium-based mineral. In addition, all the groundwater samples, had $\text{Na}^+ / [\text{Na}^+ + \text{Cl}^-]$ ratio (greater than 1.2) which may indicate that sodium sources are mainly from cation exchange and incongruent dissolution of aluminosilicate (Na-plagioclase or albite) (Adomako, 2010).

However, in Fig (4.3) the total cation versus Ca^{2+} did not show good relation with $R^2 = 0.60$. This may also confirm that the Na^+ ions are dominant over the Ca^{2+} ions in the study area. Granite rocks in study area are dominated by feldspar (Pelig-Ba, 2012).

The HCO_3^- versus $(\text{Ca}^{2+} + \text{Mg}^{2+})$ was also plotted as shown in Fig (4.5). The data observed did not indicate good relation with $R^2=0.07$ suggesting that $(\text{Ca}^{2+} + \text{Mg}^{2+})$ is not a dominant ion in study area. This may also suggest that the excess alkalinity in the water has not been balanced by the alkalis metals ($\text{Na}^+ + \text{K}^+$).

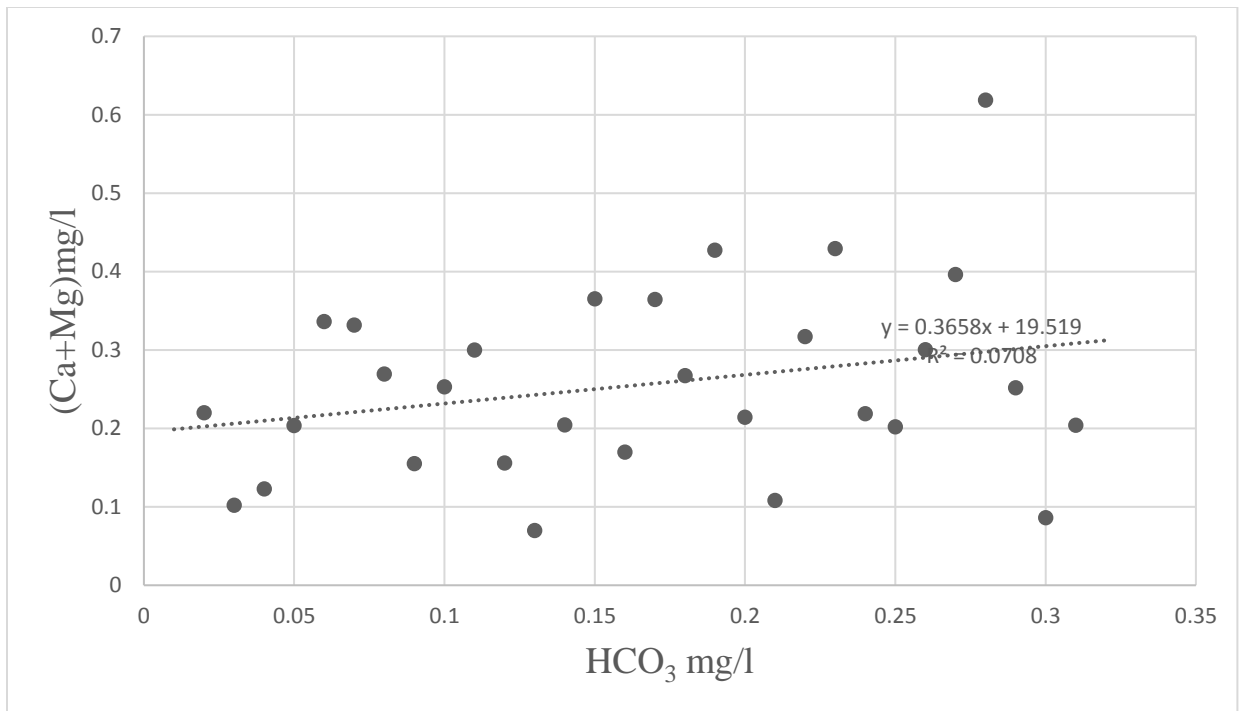


Figure 4.5 Plot of (Ca+Mg) mg/l against total cation mg/l

Again, a plot of total cations versus ($\text{Na}^+ + \text{K}^+$) [Fig. 4.6] was used to further assess the contribution of cations by silicate weathering. From the Scatter plot of total cations versus ($\text{Na} + \text{K}$) [Fig 4.6], there is a strong relation between the two. This gives the indication that these cations are from silicate weathering (Glover, 2013).

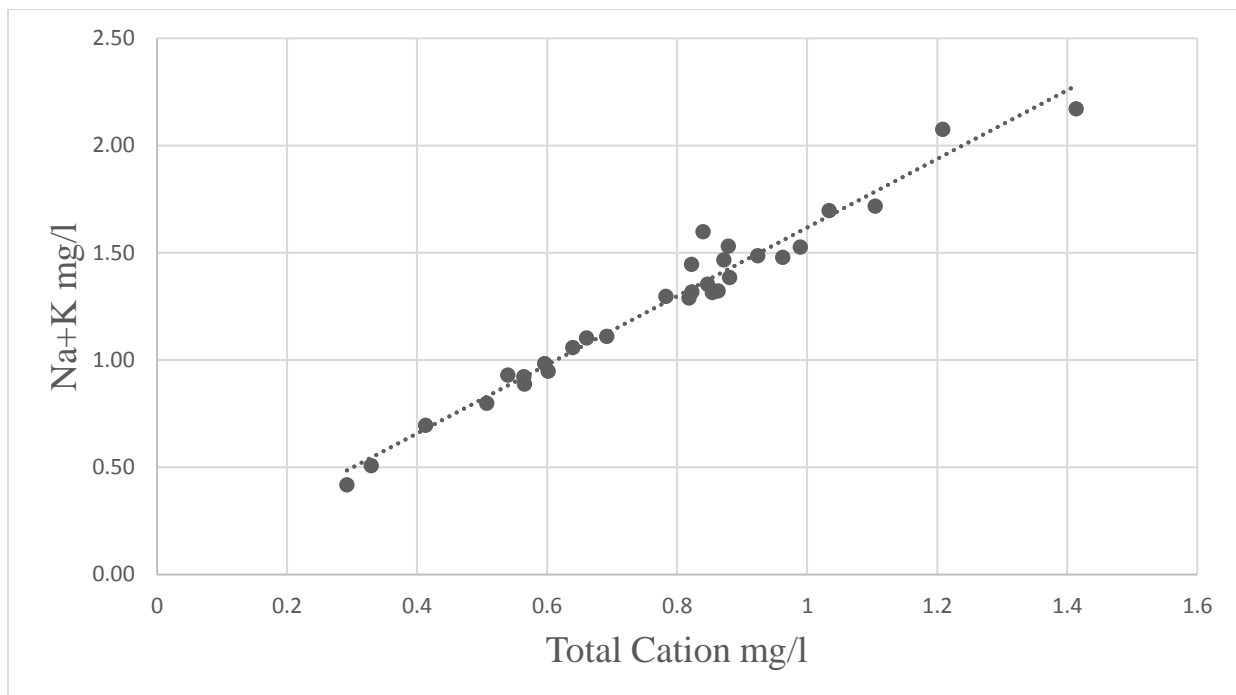


Figure 4.6 Plot of (Na+K) mg/l versus Total Cation mg/l

Furthermore, incongruent dissolution of silicate minerals may have contributed significantly to the concentrations of Mg^{2+} and Ca^{2+} ions, as shown by the plot of HCO_3^- versus total cations (TC) (Fig. 4.7). Mayo and Loucks, (1995) explained that in silicate rocks if Ca^{2+} / Mg^{2+} molar ratio is equal to one, dissolution of dolomite should occur, whereas a higher ratio is indicative of greater calcite contribution. Katz et al., (1998) also explained that the higher Ca^{2+} / Mg^{2+} molar ratio (>2) is indicative that dissolution of silicate minerals may have contributed significantly to concentration of Ca and Mg. The Ca^{2+} / Mg^{2+} ratio of the groundwater samples ranged from 7.8 to 56, this supports that Ca^{2+} and Mg^{2+} ions may have resulted from incongruent dissolution of silicate minerals.

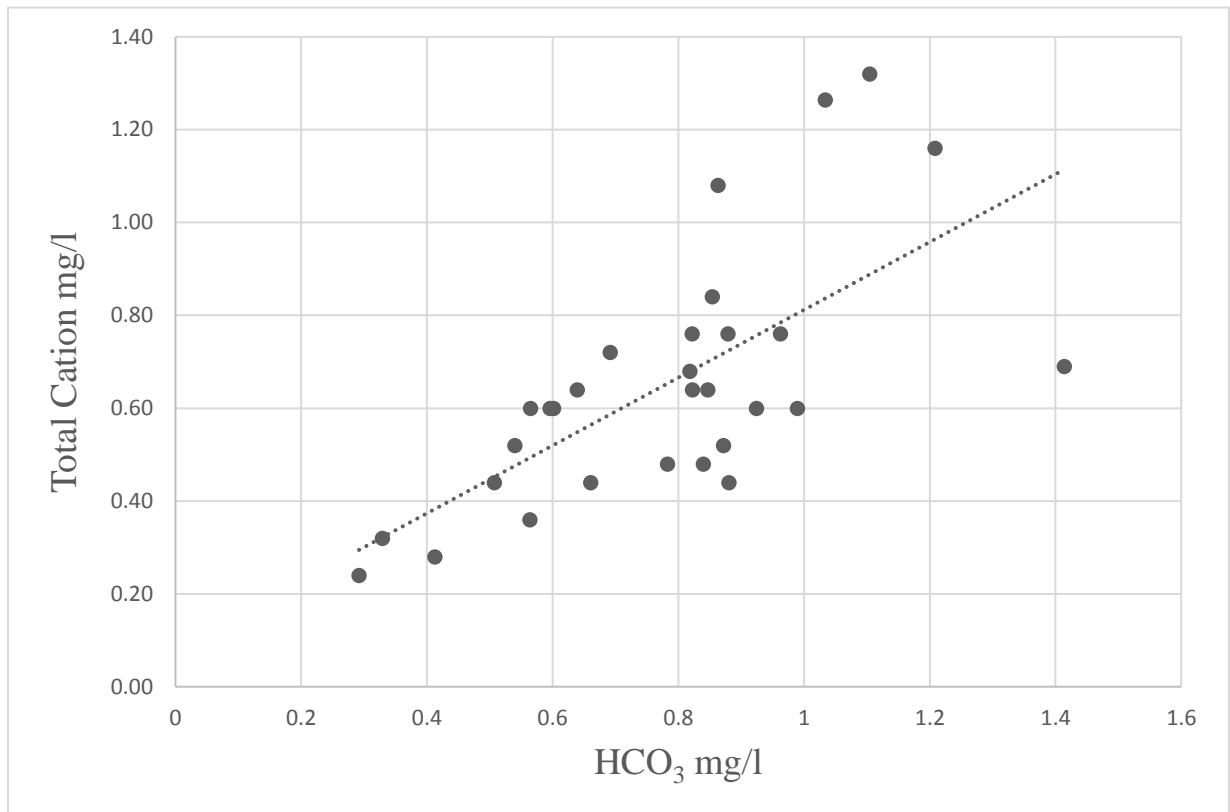


Figure 4.7 Plot of Total Cation mg/l versus HCO₃ mg/l

4.1.4 Mechanisms Controlling the Groundwater Chemistry of the Study Areas

Gibbs plot (Gibbs,1970) is the most graphical technique used to determine the hydrochemical processes that control the groundwater chemistry. Processes such as precipitation dominance, evaporation dominance and rock dominance are represented in the Gibbs diagram.

The Gibbs plot of the study area shows rock dominance and this implies that rock -water interaction is the predominant mechanisms controlling the groundwater chemistry of the

area. The interaction between rock chemistry and the chemistry of the percolation waters under the subsurface resulted into rocks weathering.

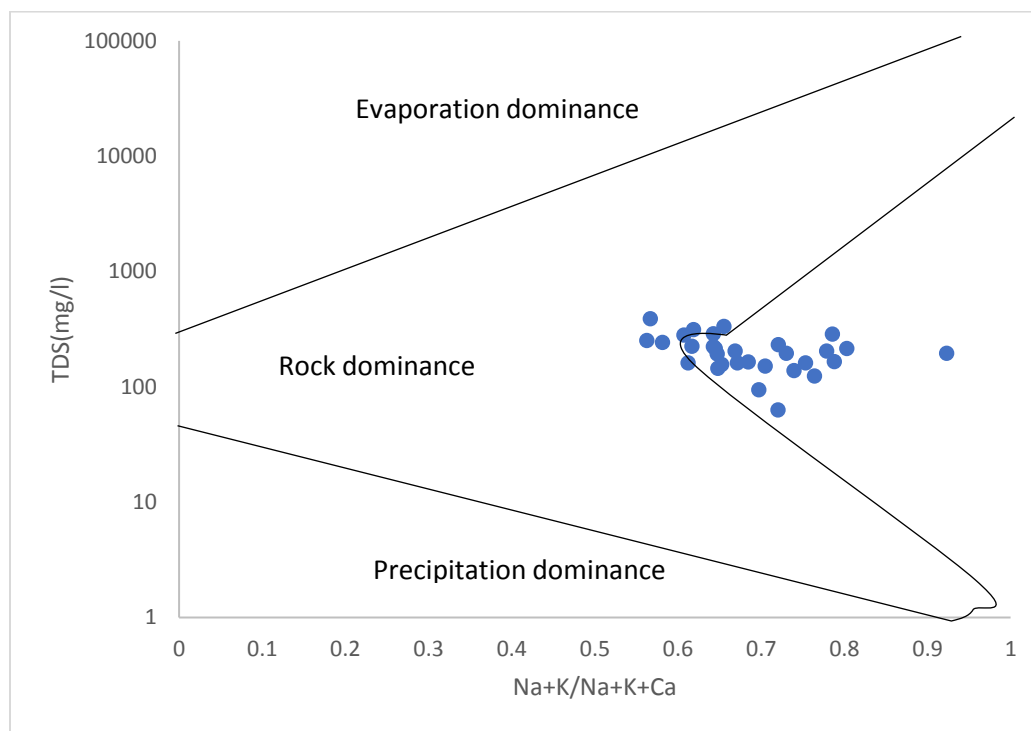


Figure 4.8 Mechanisms controlling the groundwater chemistry of the Bongo in a Gibbs plot

4.1.5 Classification of Hydrochemical Facies

The chemical component of the groundwater is indicated by major cations and anions such as Ca, Mg, Na, K, Cl, SO₄, CO₃, HCO₃, NO₃, NO₂, and PO₄. The quality of groundwater can be altered as a result of weathering and anthropogenic activities of the

The Piper plot indicated that Ca-Na+K- Cl and mixed Cl+SO₄- HCO₃ and Na+K-Ca+Mg dominated the hydrogeochemical facies of Bongo. area, (Toth in Garcia et al., 2001)

Generally, fluoride contaminated water in the study area had high concentrations of Cl^- , HCO_3^- , Na^+ and low concentration of Ca^{2+} resulting in the formation Na-K-Cl , Na_2SO_4 and Na-K-HCO_3 . Several other studies have also demonstrated that, high F^- are associated with high Cl^- , HCO_3^- , Na^+ and low concentration of Ca^{2+} (Li et al., 2018; Wu et al., 2015). In summary, the geochemical characteristics F^- in groundwater in the study area is mainly govern by the interplay of Na^+ release and Ca^{2+} removal. This imply that, the hydrochemical facies displayed in the study area is due to fluoride contaminated water. Also, the higher concentration of Cl^- in the study area could have been attributed to anthropogenic sources such as rapid increase in improper irrigation activities and animals rearing, open defecation and uncontrolled disposal of animal droppings.

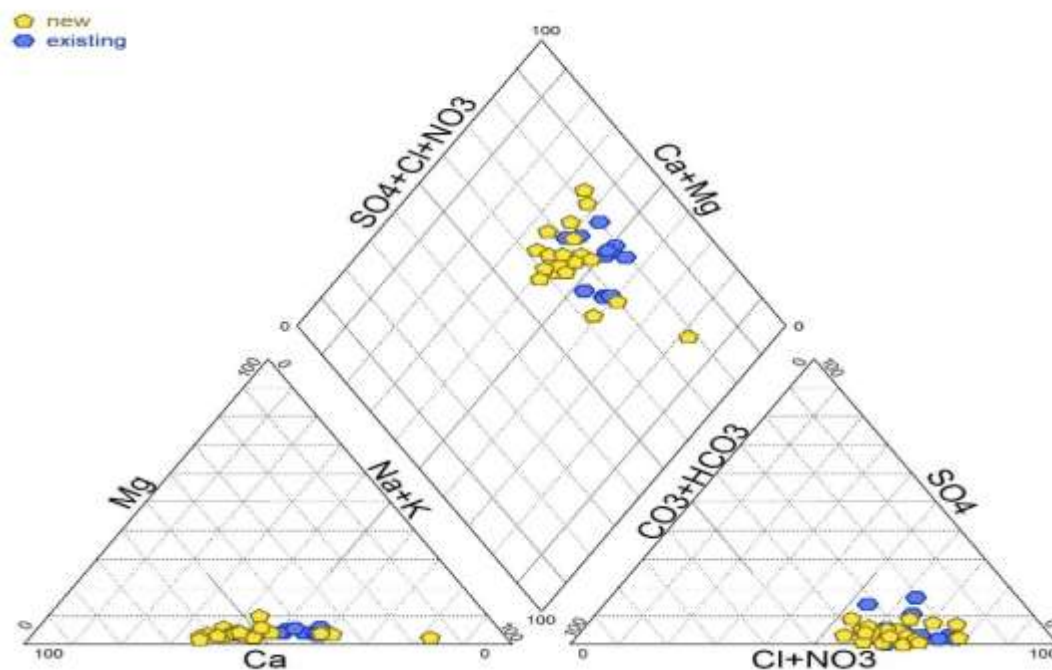


Figure 4.9 showing Piper plot of Bongo

4.1.6 Cluster Analysis

To reveal the association and alterations between the groundwater samples, statistical analysis was carried out on the physio-chemical parameters and major ion concentration. SPSS software (SPSS, 2001) was used to evaluate cluster analysis (hierarchical tree clustering, rescaled distance cluster combine analysis). The hierarchical cluster analysis was used to group water samples into significant clusters. Two different groups or clusters were discovered with respect to the geochemical parameters.

The Ward method was used to perform dendrogram analysis and the outcomes of parameters are presented in fig. Most of the samples were classified in group I with good correlation between SO_4 , Ca, HCO_3 , Cl and Na with EC and TDS. The group II with one sub-group constructed with EC and TDS. The possible salt combinations are probably derived from weathering of rock salts, gypsum-bearing aquifers and leaching of irrigation flow. The concentration of nitrate is probably derived from anthropogenic activities.

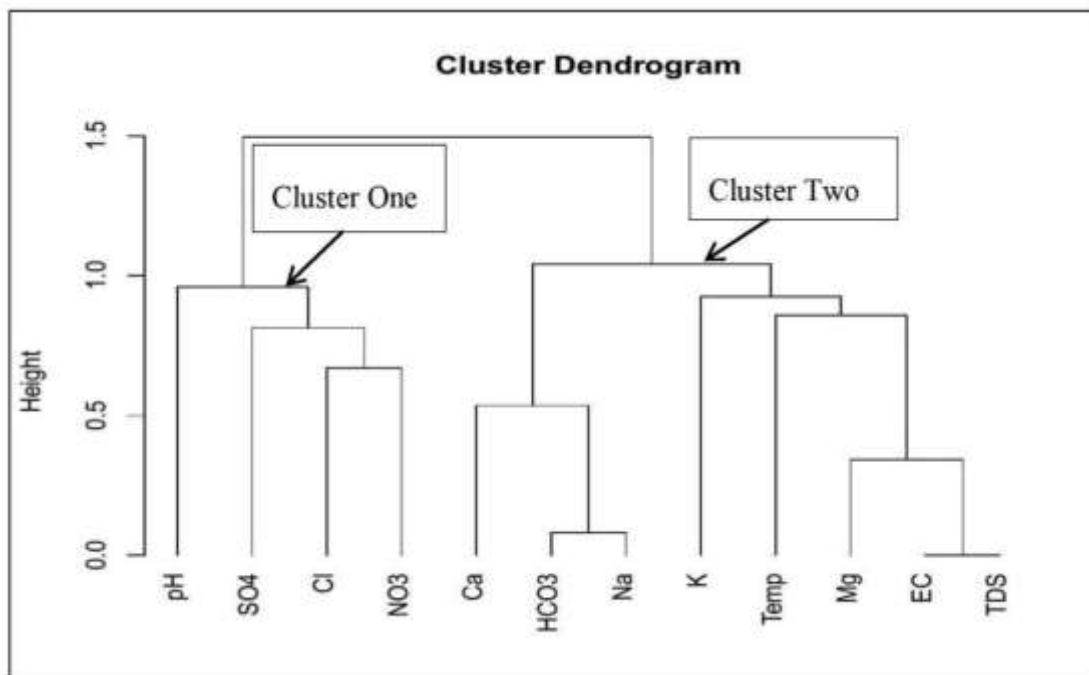


Figure 4.10. Showing Tree diagram for 12 variables measured for the geochemical studies.

The correlation matrix reveals that, the strong correlation of the hydrochemical parameters may propose some higher grade of water-rock interaction principally dissolution of minerals in rocks and soil constituents (geology) (Gibrilla et al., 2011). However, groundwater samples with classified negative correlation indicating less influence of water-rock interactions and this imply that less mineralisation might have taken place in this groundwater.

The strong correlation by Na^+ and Cl^- and weak correlation by NO_3^- and SO_4^{2-} may show that origin of Na^+ and Cl^- might be different from that of NO_3^- and SO_4^{2-} . This specifies substantial impact to a minor level as the input of anthropogenic activities like fertilizer application .

| Parameter | Temp | Ph | EC | TDS | HCO ₃ ⁻ | Cl- | SO ₄ ²⁻ | NO ₃ ⁻ | Ca | Mg | Na | K |
|-------------------------------|----------|----------|----------|----------|-------------------------------|----------|-------------------------------|------------------------------|----------|----------|----------|---|
| Temp | 1 | | | | | | | | | | | |
| PH | 0.210898 | 1 | | | | | | | | | | |
| EC | 0.042482 | 0.558863 | 1 | | | | | | | | | |
| TDS | 0.043887 | 0.557996 | 0.999989 | 1 | | | | | | | | |
| HCO ₃ ⁻ | 0.289348 | 0.551094 | 0.759305 | 0.759637 | 1 | | | | | | | |
| Cl- | -0.04363 | 0.361694 | 0.887723 | 0.888507 | 0.605837 | 1 | | | | | | |
| SO ₄ ²⁻ | 0.085156 | 0.014961 | 0.269287 | 0.268132 | -0.05346 | 0.084925 | 1 | | | | | |
| NO ₃ ⁻ | -0.07795 | 0.150807 | 0.214776 | 0.21424 | 0.076232 | 0.059747 | 0.457385 | 1 | | | | |
| Ca | 0.024808 | 0.688549 | 0.850209 | 0.849724 | 0.555889 | 0.754058 | 0.166606 | 0.125287 | 1 | | | |
| Mg | 0.097515 | 0.553613 | 0.470389 | 0.469994 | 0.497761 | 0.333682 | -0.13483 | 0.280002 | 0.482911 | 1 | | |
| Na | 0.090835 | 0.257234 | 0.781202 | 0.782212 | 0.603655 | 0.822295 | 0.237764 | 0.206357 | 0.496865 | 0.230996 | 1 | |
| K | -0.31734 | -0.07913 | 0.016049 | 0.015247 | 0.085874 | 0.135074 | -0.37192 | 0.010011 | 0.041391 | 0.194311 | -0.09791 | 1 |

Table4.2 Correlation matrix of studied physio-chemical parameters and major ions of the groundwater

4.1.7 Trace Element

The levels of trace elements (Fe, As and Mn) in all the samples were mostly low with concentrations almost below instrument detection limits.

4.1.7.1 Iron (Fe)

The iron (Fe) concentration in the water samples ranged from 0.024mg/l to 0.369mg/L with a mean value of 0.1693 mg/L for the samples. Though, 66.7% of Fe concentrations in the samples were below detection limit of 0.006 mg/L. Commonly the concentration of Fe in water samples were within recommended levels in drinking water WHO (2004).

4.1.7.2 Manganese (Mn)

The Manganese (Mn) concentration in the water samples were from 0.002 to 0.0175 mg/L with a mean value of 0.01mg/L for the samples. Though, 80.0% of Mn concentrations were below detection limit 0.002 mg/L. Commonly the concentration of Mn in water samples were within recommended levels according the World Health Organization standards WHO (2004).

4.1.7.3 Arsenic (As)

The Arsenic (As) concentration in the water samples were from 0.001 to 0.006 mg/L with a mean value of 0.003 mg/L for the samples. Though, 83.3% of As concentrations were below detection limit 0.001 mg/L. Commonly the concentration of As in water samples

were within recommended levels according the World Health Organization standards WHO (2004).

4.1.7.4 Elemental Relationship

The relationships among the trace elements were investigated by using a correlations matrix of the trace elements concentrations in the water samples. Generally, the trace elements in the samples demonstrate strong correlation between elemental pairs, except for Fe and Mn which show negative correlation, and this imply that the Fe and Mn are not from the same source. The dominant bedrock in the area are the source of the trace elements in the groundwater as propose by earlier research in the upper region (Pelig-Ba, 1998). The strong correlations between the trace elements pairs indicate to great degree that they are from a common source. This may have resulted from anthropogenic activities like fertilizer and agro-chemical application.

| | Fe | Mn | As |
|----|----------|----------|----|
| Fe | 1 | | |
| Mn | -0.13813 | 1 | |
| As | 0.934627 | 0.568682 | 1 |

Table 4.3 Pearson correlation coefficient of trace elements concentrations in groundwater at 95% confident interval

4.1.8 Water Quality

Evaluation of hydrochemical data in this study in terms of its fittingness for drinking and irrigation purposes was carried out. The standard guideline values suggested by the World Health Organisation (WHO, 2004) were used to equate with the analytical outcomes.

4.1.8.1 Water Quality Index

The water quality index (WQI) estimation was conducted by following the ‘weighted arithmetic index method’ (Brown et al. 1970), as show in the equation:

$$WQI = \frac{\sum Q_n W_n}{\sum W_n} \quad (3.11)$$

Where, Q_n is the quality rating of nth water quality parameter, W_n is the unit weight of nth water quality parameter. The quality rating Q_n is calculated using the equation

$$Q_n = 100 \frac{(V_n - V_i)}{(V_s - V_i)} \quad (3.12)$$

Where, V_n is the actual amount of nth parameter present, V_i is the ideal value of the parameter [$V_i = 0$, except for pH ($V_i = 7$)], V_s is the standard permissible value for the nth water quality parameter.

Unit weight (W_n) is calculated using the formula: $W_n = k/V_s$

where k is the constant of proportionality and it is

calculated using the equation

$$k = [1/\sum 1/V_s = 1, 2, \dots, n] .$$

The parameters used in calculating the water quality are presented in Table

| Parameter | WHO Standard Value, V_s | Ideal Value, V_i | $(V_s)^{-1}$ |
|---------------------------|---------------------------|--------------------|--------------|
| Ph | 8.5 | 7 | 0.11765 |
| EC ($\mu\text{S/cm}$) | 1200 | 0 | 00083 |
| TDS (mg/L) | 500 | 0 | 0.00200 |
| Ca^{2+} (mg/L) | 75 | 0 | 0.01333 |
| Mg^{2+} (mg/L) | 30 | 0 | 0.03333 |
| Na^+ (mg/L) | 200 | 0 | 0.00500 |
| HCO_3^- (mg/L) | 120 | 0 | 0.00833 |
| Cl^- (mg/L) | 250 | 0 | 0.00400 |
| NO_3^- (mg/L) | 50 | 0 | 0.02000 |
| SO_4^{2-} (mg/L) | 250 | 0 | 0.00400 |
| F (mg/L) | 1.5 | 0 | 0.66667 |
| Fe (mg/L) | 0.3 | 0 | 3.33333 |
| As (mg/L) | 0.01 | 0 | 100 |

Table 4.4 Water quality parameters, their standard values, their ideal values and the assigned weighting factors.

The presentation of the physio-chemical parameters selected in all the sampling sites and the corresponding WQI values are in a tabular form. Excellent, good, poor, very poor and unfit for human consumption were then used to proportion the groundwater quality of the estimated WQI values.

Table 4.5 WQI range, status and possible usage of the water sample (Brown et al. 1972)

| WQI | Water quality status (WQS) | Possible usage |
|-----------|--|--------------------------------------|
| 0-25 | Excellent | Drinking, irrigation and industrial |
| 26-50 | Good | Drinking, irrigation and industrial |
| 51-75 | Poor | Irrigation and industrial |
| 76-100 | Very poor | Irrigation |
| Above 100 | Unsuitable for drinking and fish culture | Proper treatment required before use |

It was observed that about 93.3% of the water sample fall under excellent, 3.3 % is under good and 3.3% is poor category. This implies that most of the groundwater at the study area are suitable for drinking and irrigation purposes. The 3.3% which were poor may be as result of various anthropogenic activities like unabated dumping of solid wastes by the community, agricultural run-off, lack of proper sanitation system, and the inflow of direct sewerage from residential establishments.

Table 4.6 Water quality index (WQI) classification for individual samples

| Community | ID | WQI | Descriptions |
|-------------------------------|------|----------|--------------|
| Bulungu Atukila | BG2 | 0.528525 | Excellent |
| Atiabiisi | BG3 | 0.396758 | Excellent |
| Tarongo | BG4 | 0.538424 | Excellent |
| Aberingabiisi | BG6 | 0.82221 | Excellent |
| Aberingabiisi | BG7 | 0.603934 | Excellent |
| Kadare Chips Community | BG11 | 0.213639 | Excellent |
| Feo Asebre | BG16 | 0.367815 | Excellent |
| Yidongo | BG17 | 1.842425 | Excellent |
| Anafobiisi zuen | BG20 | 0.816998 | Excellent |
| St. Anne Primary SCH | BG26 | 2.118148 | Excellent |
| Anafobisi | BG28 | 1.499364 | Excellent |
| Balunga Chips Community | BG1 | 1.074957 | Excellent |
| Kodorogo Chips Compound | BG5 | 30.58299 | Good |
| Aberingabiisi Chips Community | BG8 | 24.71955 | Excellent |
| Sambolo Basic SCH | BG9 | 24.58602 | Excellent |

| | | | |
|---------------------------|------|----------|-----------|
| Vea Kulpeliga | BG10 | 0.311492 | Excellent |
| Asakwa | BG12 | 0.308079 | Excellent |
| Boko Chips Community | BG13 | 0.484178 | Excellent |
| Awiisi | BG14 | 18.02886 | Excellent |
| Feo Chips Community | BG15 | 0.083759 | Excellent |
| Kabre | BG18 | 0.383164 | Excellent |
| Akunduo | BG19 | 0.32188 | Excellent |
| Asaloko | BG21 | 0.355362 | Excellent |
| Nabiisi | BG22 | 0.40927 | Excellent |
| Atampiisi Chips Community | BG23 | 1.25255 | Excellent |
| Bongo Snr High | BG24 | 60.05127 | Poor |
| St. Anne Primary SCH | BG25 | 1.222669 | Excellent |
| Anafobiisi Basic SCH | BG27 | 2.594647 | Excellent |
| Gowrie Kunkua | BG29 | 1.440049 | Excellent |
| Gowrie | BG30 | 0.411283 | Excellent |

4.1.9 Stable Isotope (Oxygen-18 And Deuterium)

The groundwater composition of oxygen-18 and deuterium are presented in Appendix A1

The Local Meteoric Water Line equation (LMWL) (Akiti, 1980) and the Global Meteoric Water Line (GMWL) (Coplen, 1996) were the two meteoric water line incorporated. The Local Meteoric Water

Line (Akiti, 1980) is given as;

$$\delta^2\text{H} = 7.86\delta^{18}\text{O} + 13.61 \text{ and}$$

The Global Meteoric Water Line (GMWL) is given as;

$$\delta^2\text{H} = 8\delta^{18}\text{O} + 10$$

The LMWL (Akiti, 1980) was the suitable factor for the studies since the study area lies in the Upper region of Ghana and Akiti (1980) work was in the Accra plains in the South-Eastern part and Upper Regions of Ghana. The isotopic composition results of the groundwater in the study area were plotted on $\delta^{18}\text{O}$ vrs δD diagram.

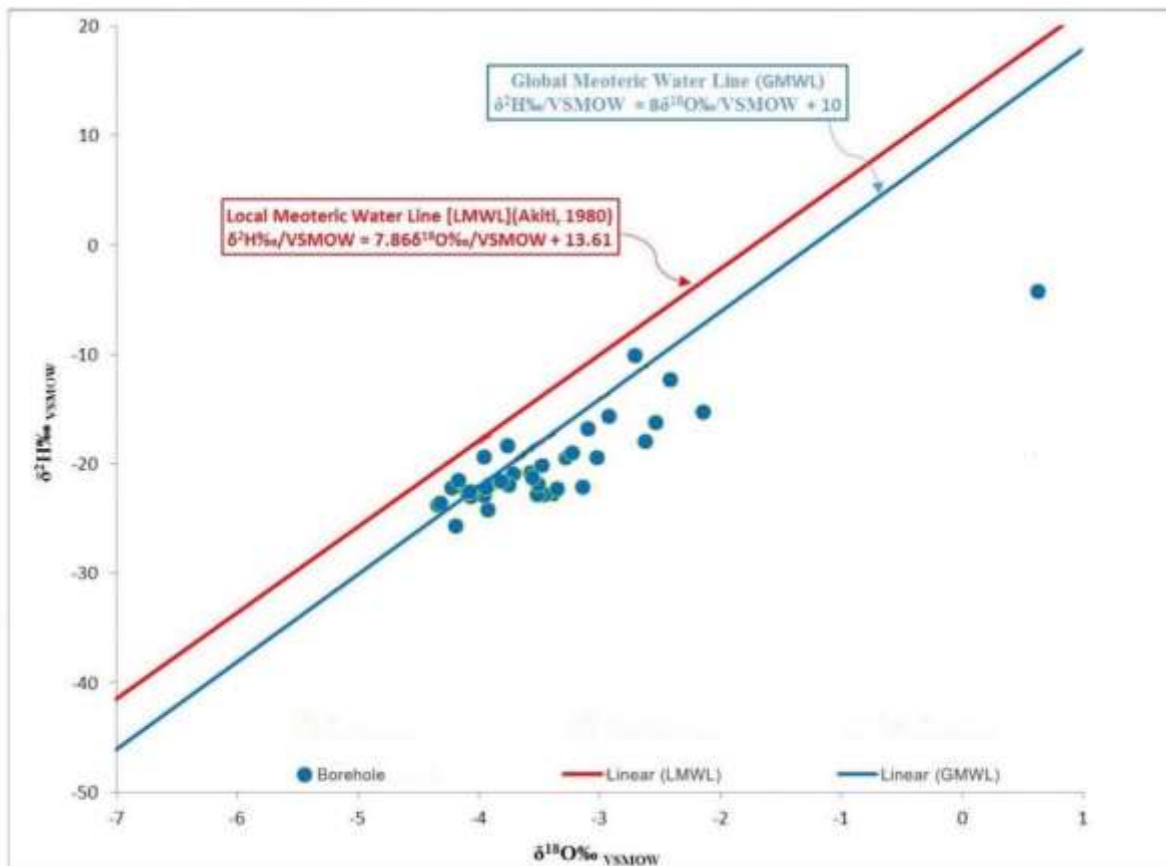


Figure 4.11 $\delta^{18}\text{O}$ – $\delta^2\text{H}$ showing relationships for isotopic composition of Akiti (1980) (LMWL), GMWL, groundwater.

4.1.9.1 Isotope composition of groundwater

The groundwater isotopic composition in the study area varied from -2.57 ‰ to -4.92 ‰ with mean isotopic content of -3.75 ‰ for $\delta^{18}\text{O}$ and from -14.86 ‰ to -29.15 ‰ with a mean isotopic composition of -20.20 ‰ for δD . Akiti (1980, 1982) reported comparable mean isotopic composition in Paga and Bolgatanga in the Upper East Region of Ghana. The isotopic composition with the maximum value -2.57 ‰ and -14.86 ‰ $\delta^{18}\text{O}$ and δD , respectively, suggested that the water have encountered a substantial evaporation before recharge and this may also imply the recharged is from an enriched source.

The useful of the effects of high temperatures, low relative humidity, slow infiltration rates and high evaporation rates over the unsaturated zone is as result of decrease in the evaporation line slope and deuterium excess than the GMWL.

Comparatively, the LMWL was higher than evaporation Line slope of the groundwater in the study area. This implies that, before recharge the infiltrating rainwater suffered some evaporation or there was distinct evaporation of raindrops. The LMWL and SWL lines intersect at a point where $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are, respectively, -26‰ and -5‰ This is the sign of the rainwater that recharged the groundwater (Akiti, 1980). However, the direct groundwater recharge from rainfall depends on the thickness and nature of the overburden material and the dominant weather conditions that directs the portion of rainfall that moves in to the saturated zone (Yidana, 2013).

The figure (4.12) agrees with Akiti (1980) that, the isotopic composition of the rainfall events giving rise to groundwater recharge has isotopic composition of -5‰ for ^{18}O and about -28‰ for ^2H . Before groundwater recharges, the groundwater has been subjected to evaporation either in the surface or in the unsaturated zone or those which stayed longer in the surface and polluted before recharge.

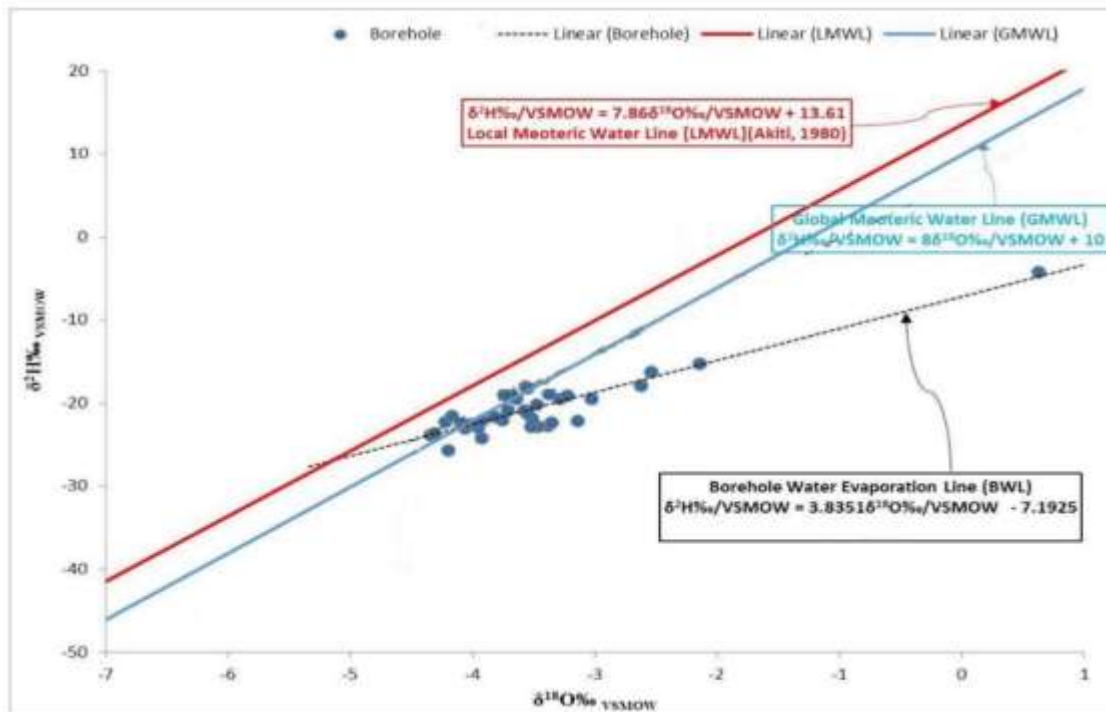


Figure 4.12: Relationship between the LMWL, GMWL and BWL in the Bongo District

4.2 Kasena-Nankana.

4.2.1 Physio-Chemical Parameters

4.2.1.1 pH

The pH values ranged from 6.05 – 7.92 with mean value of 6.85 for Kasena-Nankana West District. The groundwater in the area were near neutral to slightly alkaline and this may imply the groundwater is of granitic environment, as suggested in the previous works done in the study areas, (Akiti, 1980, 1982; Martin, 2006; Pelig-Ba, 1998). The pH of neutral water are regulated by reactions including the consumption of hydrogen and hydroxyl ions, where by the reactions can be determined by the temperature, the geology, soil type and the solubility of the bedrock, (Hill, 2000). Again, the dissolution of silicate

and carbonates minerals in groundwater in granitic environment may be near alkaline, (Pelig-Ba, 1987). This could also mean that areas with groundwater exhibiting pH <6.5 have soft and corrosive water which could leach metal ions. However, most of the samples analysed have pH values within the WHO (1993) recommended limit for portable water, 6.5 – 8.5.

4.2.1.2 Total Dissolved Solids (TDS) and Electrical Conductivity (EC)

The TDS of the samples are in the ranged of 144 mg/L of 590 mg/L, with a mean value of 271.24 mg/L. The electrical conductivity (EC) value ranged from 261 $\mu\text{S}/\text{cm}$ to 1074 $\mu\text{S}/\text{cm}$, with a mean value of 492 $\mu\text{S}/\text{cm}$. Generally, low TDS and EC values are as a result of short residence time of the groundwater or slow disintegration of granitic rock in the study areas as suggested by (Kortasi 2004). This means that almost all the groundwater from the areas, are fresh water since the TDS values of the study areas are less than 1,000 mg/l (Davis and Wiest, 1996). Except the study area KNW27 which recorded TDS value higher than the recommended limit of the drinking water, WHO (2004).

4.2.1.3 Temperature

Groundwater temperature variation recorded in the study area ranged from 31.1 °C to 35.1 °C, with a mean value of 32.4 °C. The distinctions in temperature can be due to several factors such as different sampling time, the season and, the flow and well depth (Chapman and Kimstash, 1996).

4.2.2 Hydrochemistry of Groundwater

The solubility of the minerals is typically driven by the action of carbon dioxide (Appelo and Postma, 1996b; Drever, 1982b). Also, the release of ions into groundwater generally varies with temperature, the relative solubilities, rate of supply of H⁺ and reaction kinetics of the minerals, (Adomako, 2010). The basic chemistry of groundwater samples with respect to presence of some vital cations (Ca²⁺, Mg²⁺, Na⁺ and K⁺) and anions (SO₄²⁻, HCO₃⁻ and Cl⁻) was used to investigate processes accounting for the levels in groundwater in this study.

A statistical summary of hydro-chemical parameters in Bongo is presented in table 4.7

Table: 4.7 Descriptive Statistical summary of hydrochemical parameters of Kassena Nankana West District.

| Parameter | Minimum | Maximum | Mean | WHO 2004 | MPL |
|-------------------------------|---------|---------|--------|-------------|-----|
| EC | 261.0 | 1074 | 492 | | |
| Ph | 6.05 | 7.92 | 6.85 | 6.5-8.5 | |
| TDS | 144 | 389 | 271.24 | - | |
| Temp | 31.10 | 35.10 | 32.4 | | |
| HCO ³⁻ | 32.0 | 128.0 | 88.39 | 380 | |
| Ca | 8.40 | 65.10 | 27.91 | 200 | |
| Mg | 0.59 | 1.39 | 1.18 | 150 | |
| Na | 23.60 | 215.90 | 66.61 | 200 | |
| K | 0.20 | 8.71 | 2.73 | 30 | |
| F ⁻ | 0.11 | 4.27 | 1.17 | 1.5 | |
| Cl ⁻ | 34.10 | 298.87 | 84.39 | 250 | |
| NO ₃ ⁻ | 0.99 | 28.73 | 6.78 | 10 | |
| PO ₄ ³⁻ | 0.01 | 3.38 | 0.54 | - | |
| SO ₄ ²⁻ | 0.01 | 6.85 | 2.95 | 400 | |

4.2.2.1 Major and minor ions

Na^+ is the most dominant cation in the major cations concentrations in Kasena Nankana. The order of abundance of the cations is Na^+ , Ca^{2+} , K^+ , Mg^{2+} , respectively. The higher concentration of K^+ more than Mg^{2+} may be due to the use of potassium fertilizer from agriculture.

The concentration of Na^+ in the study area ranges from 23.60 mg/L to 215.90 mg/L, with a mean value of 61.66 mg/l. 99 % of the Na^+ samples are less than the WHO (2004) permissible limit of drinking water standard except borehole KNW 27 at Akania where the Na^+ concentration is 215.90 mg/l.

The Ca^+ concentration ranges from 8.40 mg/l to 65.60 mg/l , with a mean value of 27.91 mg/l and Ca^+ was within the permissible limit of drinking water. As per drinking water standard WHO (2004), Mg^{2+} and K^+ are within the desirable limit with mean values of 1.18 mg/l and 2.73 mg/l, respectively.

Also, the relative abundance of the anions is $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^-$, with HCO_3^- being the most dominant anion. The HCO_3^- concentration ranges from 32.0 mg/l to 128.0 mg/l, with a mean value of 88.39 mg/l and HCO_3^- within the permissible limit of drinking water. The higher level of HCO may be due to enriched biogenic CO_2 in rainwater in the soil zone which destructively might have reacted with silicate minerals in the study area.

The concentration of Cl^- in the study area ranges from 34.10 mg/l to 298.87 mg/l with mean value of 84.39 mg/l. Almost all the Cl^- samples are less than the WHO (2004)

permissible limit of drinking water standard, except borehole KNW 27 at Akania where the concentration of Cl^- is 298.67 mg/l.

As per drinking water standard (WHO 1993), NO_3^- and SO_4^{2-} are within the desirable limit with mean values of 6.78 mg/l and 2.95 mg/l, respectively, except borehole KNW 14 at Mirigu CHIPS Compound, borehole KNW 13 at Mirigu CHIPS Compound and borehole KNW 11 at Kassena Nankana West Health Center where the concentration of NO_3^- is above drinking water standard WHO (2004).

The higher concentrations of Na^+ , Cl^- and NO_3^- above drinking water standard WHO (2004) observed in some of the boreholes in the study areas are suspected to be as related to pollution by human and animal waste, or fertiliser run-off.

The levels of F^- varied from 0.11 mg/L to 4.27 mg/L, with an average of 1.17 mg/L. The high fluoride concentrations were found in Naveem (2.10 mg/L), Kalivio CHPS compound (3.70 mg/L), Akania (4.27 mg/L), Aneo (1.89 mg/L), Kalivio Gugoro (2.37 mg/L) and Banyui (2.15 mg/L). This represents about 17 % of the sampled groundwater and the rest of the samples are within the permissible limit of drinking water standard WHO (2004). Generally, fluoride contaminated water in the study area had high concentrations of Cl^- , HCO_3^- , Na^+ and low concentration of Ca^{2+} resulting in the formation Na-K-Cl, Na SO_4 and Na-K- HCO_3 . Several other studies have also demonstrated that, high F^- are associated with high Cl^- , HCO_3^- , Na^+ and low concentration of Ca^{2+} (Li et al., 2018; Wu et al., 2015). PO_4^{3-} ions concentration in the groundwater generally were low.

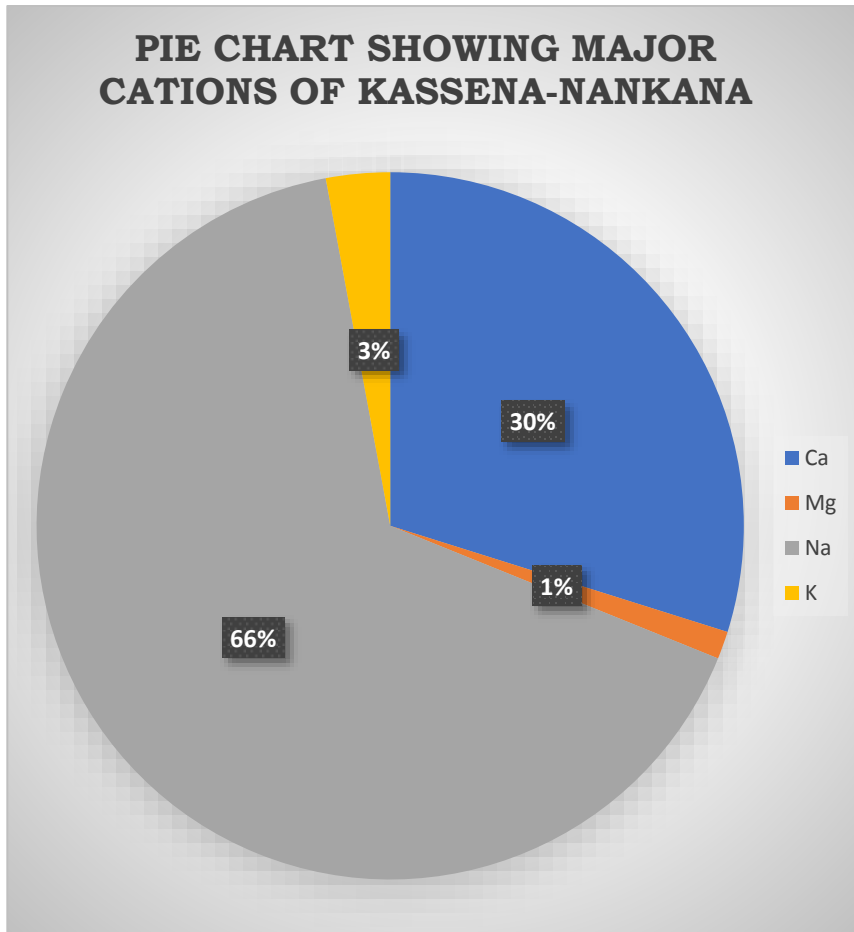


Figure 4.13 Major cations in Kassena Nankana West District

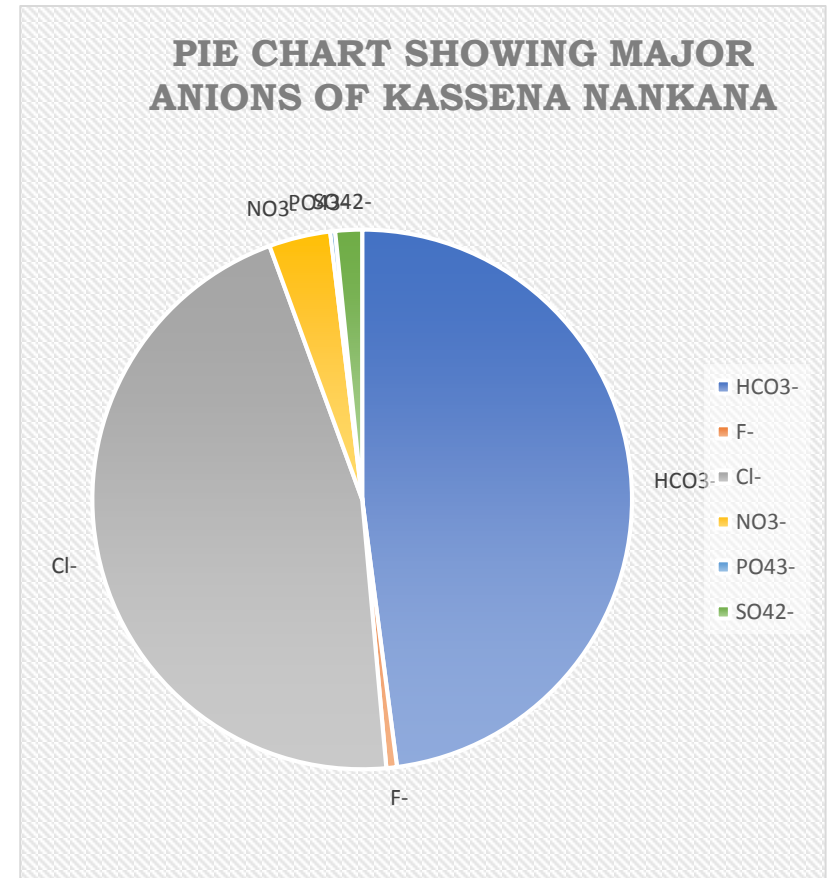


Figure 4.14 Major anions in Kassena Nankana West District

4.2.3 Mineralisation Process

To identify the origin and the processes of groundwater mineralization, bivariate plots were used to investigate the compositional relations among the dissolved ions. An examination was made by the stoichiometric relation of the major ions Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , NO_3^- observed in groundwater in the study area. Fig. 4.15 and 4.16 shows the plots of the sum of cations (Σ cations) versus Na^+ and Ca^{2+} , respectively.

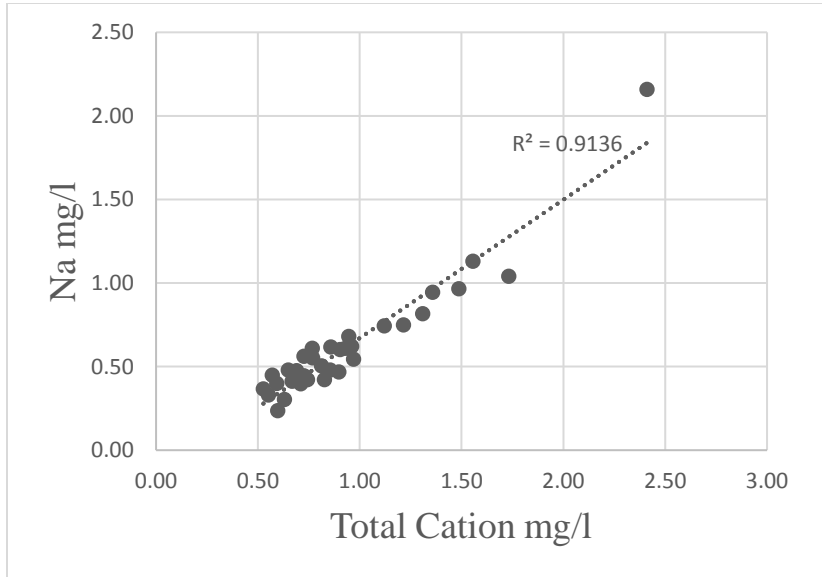


Figure 4.15 Plot of Total Cations mg/l versus Na mg/l

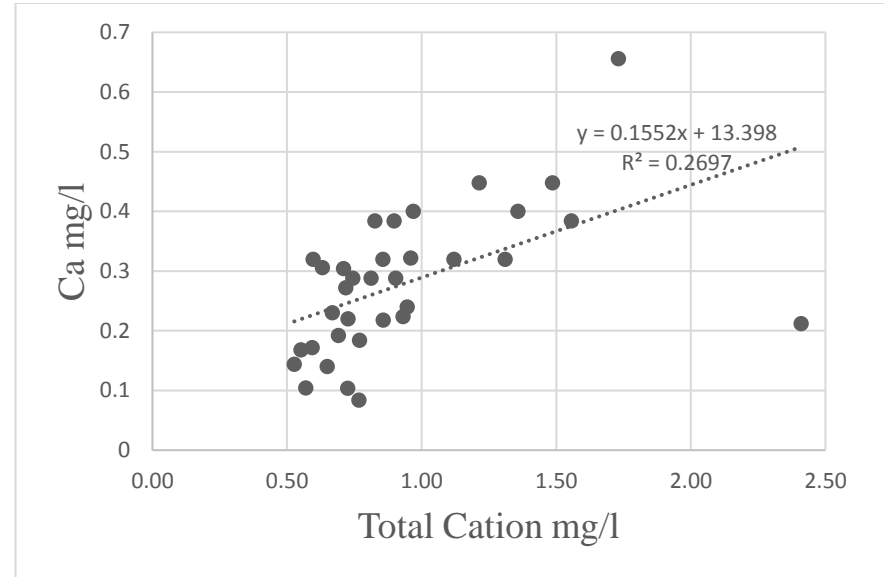


Figure 4.16 Plot of Total Cations mg/l versus Ca mg/l

A plot of Na^+ (mg/L) against total cations (mg/L) from (fig 4.15) showed strong correlation implying sodium-based mineral. In addition, all the groundwater samples, had $\text{Na}^+ / [\text{Na}^+ + \text{Cl}^-]$ ratio (greater than 0.6) which may indicate that sodium sources are mainly from cation exchange and incongruent dissolution of aluminosilicate (Na-plagioclase or albite) (Adomako, 2010). However, in Fig. (4.16) the total cation versus Ca^{2+} did not show good relation with $R^2 = 0.3$. This may also confirm that the Na^+ ions are dominant over the Ca^{2+} ions in the study area. Granite rocks in the study area are dominated by feldspar (Pelig-Ba, 2012).

The HCO_3^- versus $(\text{Ca}^{2+} + \text{Mg}^{2+})$ was also plotted as shown in Fig (4.17). The data observed did not indicate good relation with $R^2=0.03$ suggesting that $(\text{Ca}^{2+} + \text{Mg}^{2+})$ is not a dominant ion in study area. This may also suggest that the excess alkalinity in the water has not been balanced by the alkalis metals ($\text{Na}^+ + \text{K}^+$).

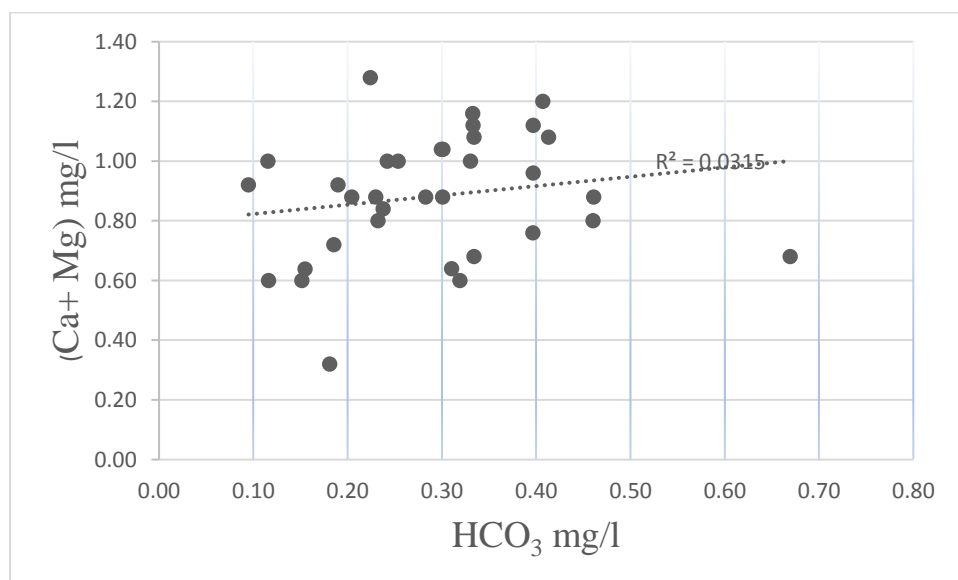


Figure 4.17 Plot HCO_3^- versus $(\text{Ca}^{2+} + \text{Mg}^{2+})$ in mg/L

Again, a plot of total cations versus ($\text{Na}^+ + \text{K}^+$) was used to further assess the contribution of cations by silicate weathering. The Scatter plot of total cations versus ($\text{Na} + \text{K}$) [Fig 4.18], indicated a strong relation between the two. This gives the indication of these cations are from silicate weathering (Glover, 2013).

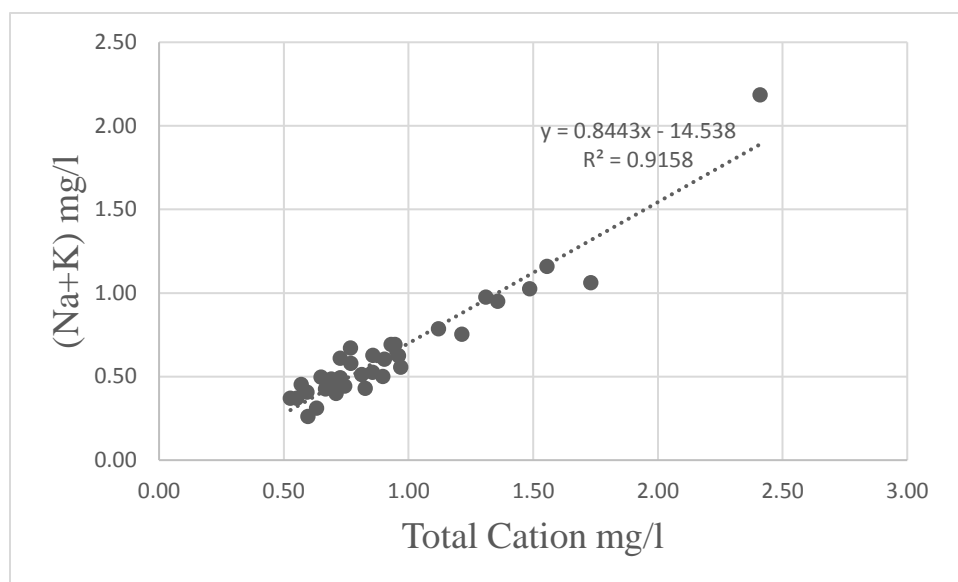


Figure 4.18 Plot ($\text{Na}^+ + \text{K}^+$) versus Total cation.

Furthermore, incongruent dissolution of silicate minerals may have contributed significantly to the concentrations of Mg^{2+} and Ca^{2+} ions, as shown by the plot of HCO_3^- versus total cations (TC) (Fig. 4.19). Mayo and Loucks, (1995) explained that, in silicate rocks, if $\text{Ca}^{2+} / \text{Mg}^{2+}$ molar ratio is equal to one, dissolution of dolomite should occur, whereas a higher ratio is indicative of greater calcite contribution. Katz et al., (1998) also explained that the higher $\text{Ca}^{2+} / \text{Mg}^{2+}$ molar ratio (>2) is indicative that dissolution of silicate minerals may have contributed significantly to concentration of Ca and Mg. The $\text{Ca}^{2+} / \text{Mg}^{2+}$ ratio of the groundwater samples

ranged from 7.7 to 57; this supports that Ca^{2+} and Mg^{2+} ions may have resulted from incongruent dissolution of silicate minerals.

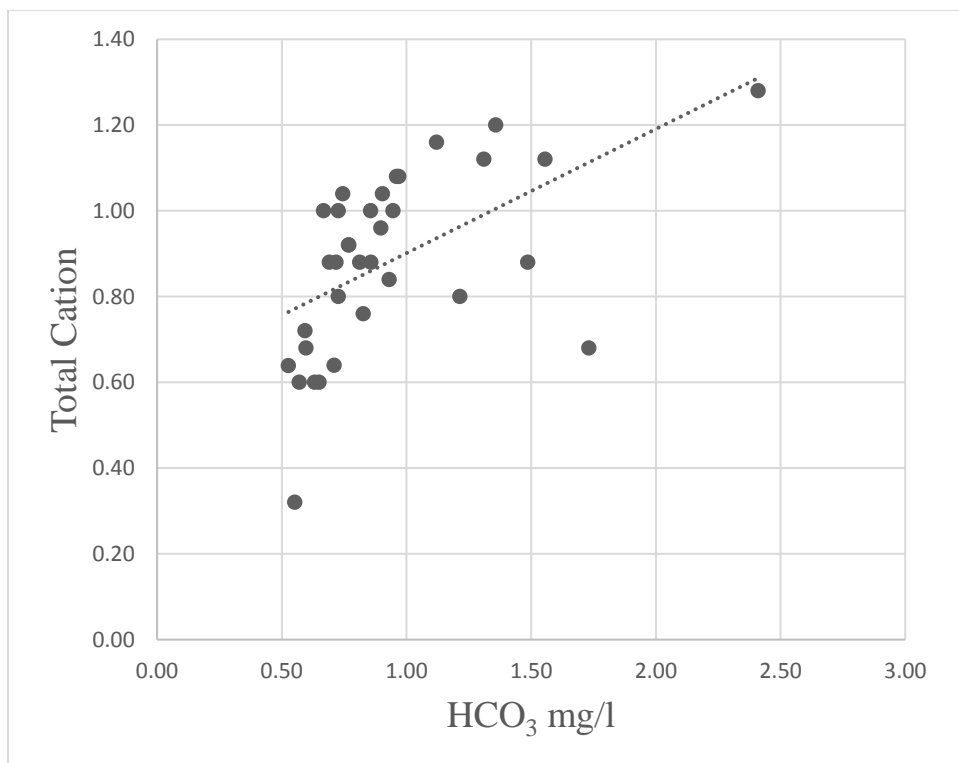


Figure 4.19 Plot of HCO_3 versus Total cations.

4.2.4 Mechanisms Controlling the Groundwater Chemistry of the Study Area

Gibbs plot (Gibbs, 1970) is the most analytical technique used to determine the hydrochemical processes that control the groundwater chemistry. Processes such as precipitation dominance, evaporation dominance and rock dominance are represented in the Gibbs diagram.

The Gibbs plot of the study areas, as represented in Fig (4.20) shows rock dominance and this implied that, rock-water interaction is the predominant mechanism controlling the

groundwater chemistry of the areas. The interaction between rock chemistry and the chemistry of the percolation waters under the subsurface resulted into rocks weathering.

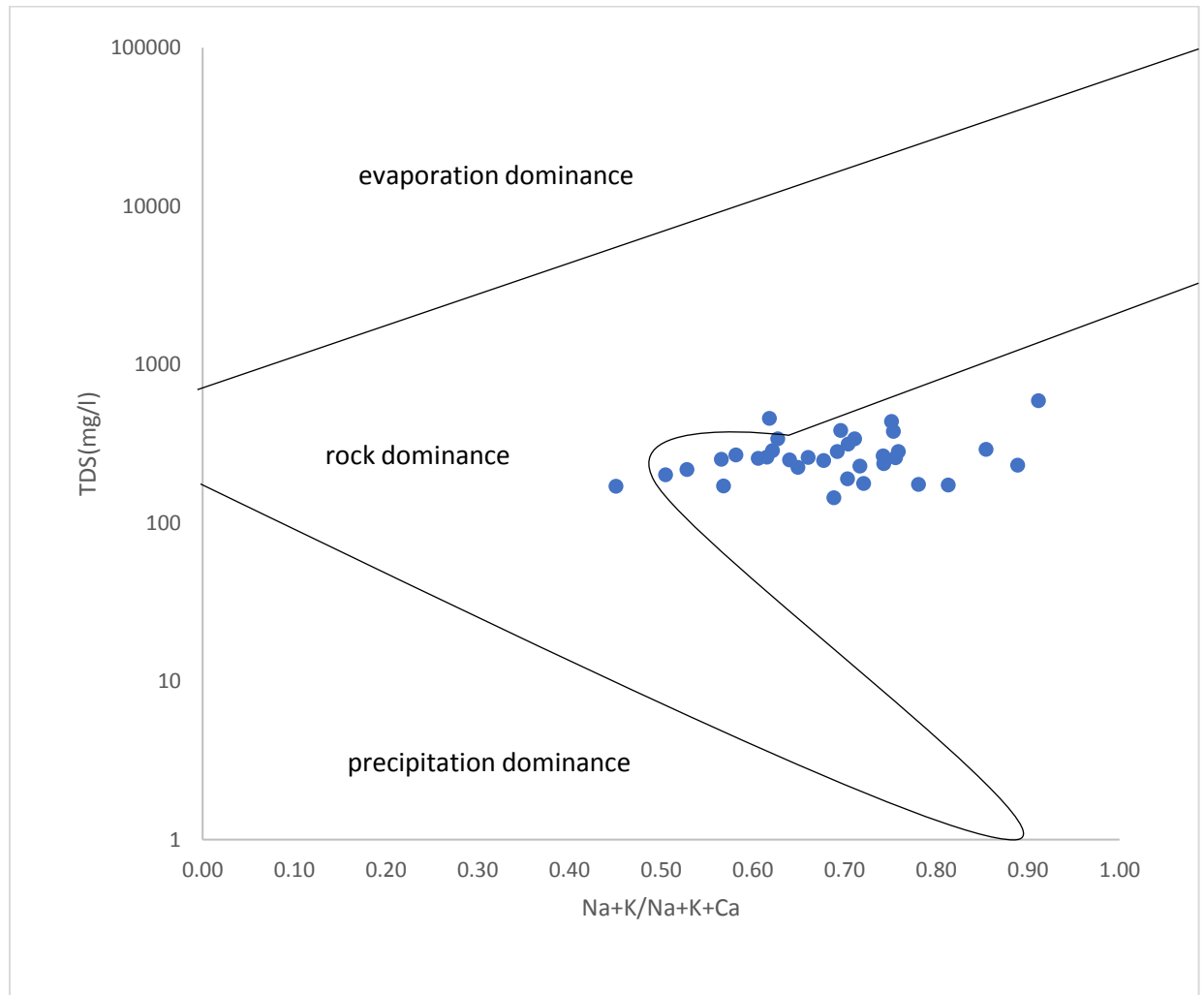


Figure 4.20 Mechanisms controlling the groundwater chemistry of the Kassena Nankana West District in a Gibbs plot

4.2.5 Classification of Hydrochemical Facies

Alterations in hydrochemical characteristics of groundwater in different places may be due to geologic structures and hydrogeological settings. The chemistry and classification of groundwater with respect to vital cations and anions such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} ,

HCO_3^- , Cl^- , NO_3^- and SO_4^{2-} , respectively, was examined with Piper Trilinear plot (Piper, 1944). The main hydrochemical types in the study area is Ca-Na+K- HCO_3^- - Cl and Cl+ SO_4^- - HCO_3^- mixed water.

Generally, there is very little or absence of Cl ion in the groundwater of the Upper Region. The higher concentration of Cl^- in the study area could have been attributed to anthropogenic sources such as increased population, rapid increase in irrigation activities and animals rearing, open defecation and uncontrolled disposal of animal droppings

It may also come from geochemical processes and chemical reactions leading to interplay of Na^+ release and Ca^{2+} removal Li et al. (2018).

Several other studies have also demonstrated that, high F^- are associated with high Cl^- , HCO_3^- , Na and low concentration of Ca^{2+} (Li et al., 2018; Wu et al., 2015). This imply that, the high concentrations of Cl^- , HCO_3^- , Na^+ and low concentration of Ca^{2+} in the hydrochemical facies is due to fluoride contaminated water in the study area

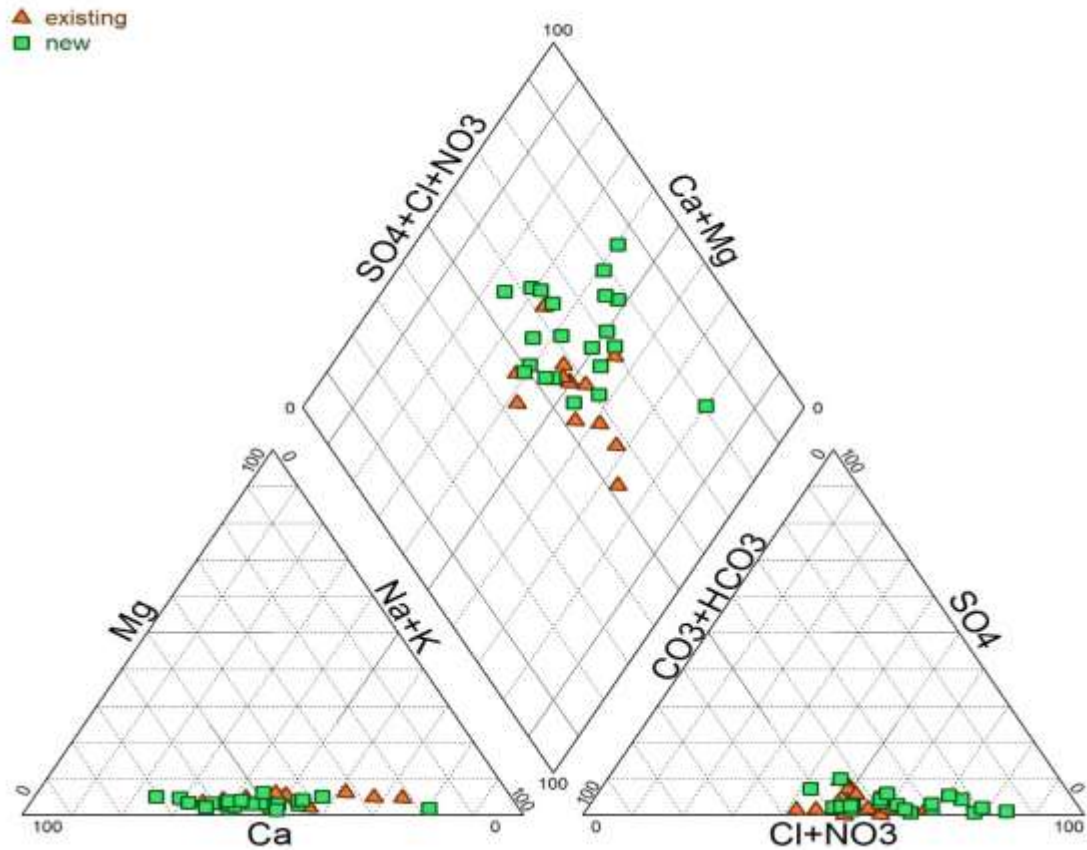


Figure 4.21 Piper plot showing the hydrochemical facies in Kassena Nankana west

4.2.6 Cluster Analysis

To reveal the association and alterations between the groundwater samples, statistical analysis was carried out on the physio-chemical parameters and major ion concentration. SPSS software (SPSS, 2001) was used to evaluate cluster analysis (hierarchical tree clustering, rescaled distance cluster combine analysis). The hierarchical cluster analysis was used to group water samples into significant clusters. Two different groups or clusters was discovered with respect to the geochemical parameters.

The Ward method was used to performed dendrogram analysis and the outcomes of parameters are presented in Fig (4.22). Most of the samples were classified in group I with good correlation between SO_4^{2-} , Ca, HCO_3^- , Cl and Na with EC and TDS. The group II with one sub-group constructed with EC and TDS. The possible salt combinations are probably derived from weathering of rock salts, gypsum-bearing aquifers and leaching of irrigation flow. The concentration of nitrate is probably derived from anthropogenic activities.

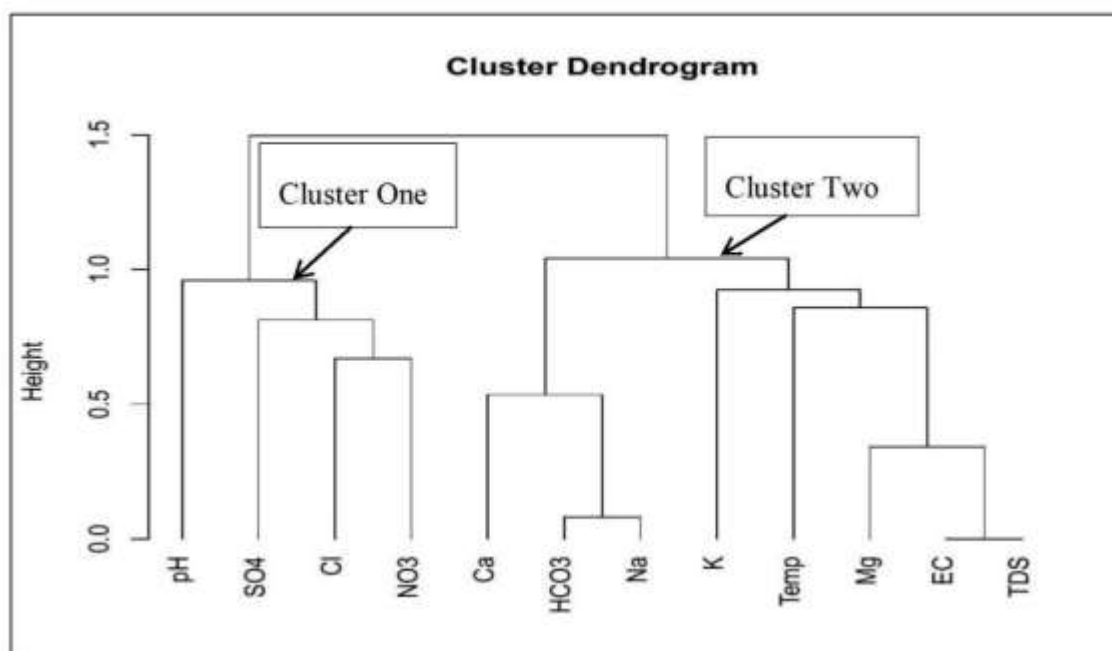


Figure 4.22: Tree diagram for 12 variables measured for the geochemical studies

The correlation matrix shows that, the strong correlation of the hydrochemical parameters may suggests some higher grade of water-rock interaction principally dissolution of minerals in rocks and soil constituents (geology) (Gibrilla et al., 2011). However, groundwater samples with negative correlation indicating less influence of water-rock

interactions and this imply that less mineralisation might have taken place in this groundwater.

The strong correlation between Na^+ and Cl^- and weak correlation between NO_3^- and SO_4^{2-} may show that origin Na^+ and Cl^- might be different from that of NO_3^- and SO_4^{2-} . This indicates substantial impact to a minor level as the input of anthropogenic activities like fertilizer application.

| Parmeter | pH | EC | TDS | Temp | HCO ₃ ⁻ | Ca | Mg | Na | K | F ⁻ | Cl ⁻ | NO ₃ ⁻ | PO ₄ ³⁻ | SO ₄ ²⁻ |
|-------------------------------|----------|----------|----------|----------|-------------------------------|----------|----------|----------|----------|----------------|-----------------|------------------------------|-------------------------------|-------------------------------|
| pH | 1 | | | | | | | | | | | | | |
| EC | 0.276676 | 1 | | | | | | | | | | | | |
| TDS | 0.282789 | 0.999437 | 1 | | | | | | | | | | | |
| Temp | 0.002103 | -0.20106 | -0.20014 | 1 | | | | | | | | | | |
| HCO ₃ ⁻ | 0.463803 | 0.610169 | 0.613334 | -0.09903 | 1 | | | | | | | | | |
| Ca | 0.156111 | 0.46054 | 0.461765 | -0.22307 | 0.179071 | 1 | | | | | | | | |
| Mg | 0.052419 | 0.106752 | 0.102005 | 0.049255 | -0.06266 | 0.160713 | 1 | | | | | | | |
| Na | 0.223289 | 0.913314 | 0.910667 | -0.2264 | 0.555296 | 0.25664 | 0.031652 | 1 | | | | | | |
| K | 0.040185 | 0.286917 | 0.290414 | 0.300594 | 0.196774 | -0.03435 | 0.195814 | 0.163062 | 1 | | | | | |
| F ⁻ | -0.00541 | 0.299406 | 0.299258 | -0.18727 | 0.275753 | -0.33264 | -0.157 | 0.543349 | -0.0156 | 1 | | | | |
| Cl ⁻ | 0.145626 | 0.906371 | 0.902343 | -0.20005 | 0.418328 | 0.509341 | 0.07965 | 0.913973 | 0.226879 | 0.343566 | 1 | | | |
| NO ₃ ⁻ | 0.567716 | 0.471681 | 0.473646 | -0.06774 | 0.268701 | 0.282237 | 0.232103 | 0.393762 | -0.00616 | -0.05894 | 0.300652 | 1 | | |
| PO ₄ ³⁻ | -0.14983 | 0.460964 | 0.456754 | -0.09956 | 0.135786 | -0.1327 | 0.020121 | 0.581045 | -0.03192 | 0.50361 | 0.50853 | 0.034255 | 1 | |
| SO ₄ ²⁻ | -0.43231 | 0.055301 | 0.051282 | -0.18741 | -0.09423 | -0.00417 | 0.033375 | 0.125606 | -0.09086 | 0.14163 | 0.148222 | -0.22539 | 0.25543 | 1 |

Table4.8 Correlation matrix of studied physio-chemical parameters and major ions of the groundwater

4.2.7 Trace Element

The levels of trace elements (Fe, As and Mn) in all the samples were mostly low with concentrations almost below instrument detection limits.

4.2.7.1 Iron (Fe)

The iron (Fe) concentration in the water samples ranged from 0.006 to 0.80mg/L with a mean value of 0.26 mg/L. Though, 37.5 % of Fe concentrations in the samples were below detection limit of 0.006 mg/L, the concentration of Fe in water samples were within recommended levels in drinking water WHO (2004).

4.2.7.2 Manganese (Mn)

The Manganese (Mn) concentration in the water samples were from 0.002 to 0.24 mg/L with a mean value of 0.04mg/L. Though, 46.9 % of Mn concentrations were below detection limit 0.002 mg/L, the concentration of Mn in water samples were within recommended levels according the World Health Organization standards WHO (2004).

4.2.7.3 Arsenic (As)

The Arsenic (As) concentration in the water samples were from 0.001 to 0.006 mg/L with a mean value of 0.003 mg/L for the samples. Though, 84.4% of As concentrations were below detection limit 0.001 mg/L, the concentration of As in water samples were within recommended levels according the World Health Organization standards WHO (2004).

2.6.8 Elemental Relationship

The relationships among the trace elements were investigated by using a correlations matrix of the trace elements concentrations in the water samples. Generally, the trace elements in the samples demonstrate poor correlation between elemental pairs; Fe and Mn, Fe and As. The dominant bedrock in the area are the source of the trace elements in the groundwater as recommend by earlier research in the upper region (Pelig-Ba, 1998). The weak correlations between the trace elements pairs indicate to less degree that they are not from a common source. This may have resulted from anthropogenic activities.

| | Fe | Mn | As |
|----|----------|----------|----|
| Fe | 1 | | |
| Mn | 0.073705 | 1 | |
| As | -0.46031 | 0.282106 | 1 |

Table 4.9 Pearson correlation coefficient of trace elements concentrations in groundwater at 95 % confident interval.

4.2.9 Water Quality

Evaluation of hydrochemical data in this study in terms of its fittingness for drinking and irrigation purposes was carried out. The standard guideline values suggested by the World Health Organisation (WHO, 2004) were used to equate with the analytical outcomes.

4.2.9.1 Water Quality Index

The water quality index (WQI) estimation was conducted by following the ‘weighted arithmetic index method’ (Brown et al. 1970), as show in the equation:

$$WQI = \frac{\sum Q_n W_n}{\sum W_n}$$

Where, Q_n is the quality rating of nth water quality parameter, W_n is the unit weight of nth water quality parameter. The quality rating Q_n is calculated using the equation

$$Q_n = 100 \frac{(V_n - V_i)}{(V_s - V_i)}$$

where V_n is the actual amount of nth parameter present, V_i is the ideal value of the parameter [$V_i = 0$, except for pH ($V_i = 7$)], V_s is the standard permissible value for the nth water quality parameter.

Unit weight (W_n) is calculated using the formula: $W_n = k/V_s$

Where, k is the constant of proportionality and it is

calculated using the equation

$$k = [1/\sum 1/V_s = 1, 2, \dots, n].$$

The parameters used in calculating the water quality are presented in Table (4.10)

Table 4.10: Water quality parameters, their standard values, their ideal values and the assigned weighting factors.

| Parameter | WHO Standard Value, V_s | Ideal Value, V_i | $(V_s)^{-1}$ |
|--------------------------------|---------------------------|--------------------|--------------|
| Ph | 8.5 | 7 | 0.11765 |
| EC ($\mu\text{S}/\text{cm}$) | 1200 | 0 | 00083 |
| TDS (mg/L) | 500 | 0 | 0.00200 |
| Ca^{2+} (mg/L) | 75 | 0 | 0.01333 |
| Mg^{2+} (mg/L) | 30 | 0 | 0.03333 |
| Na^+ (mg/L) | 200 | 0 | 0.00500 |
| HCO_3^- (mg/L) | 120 | 0 | 0.00833 |
| Cl^- (mg/L) | 250 | 0 | 0.00400 |
| NO_3^- (mg/L) | 50 | 0 | 0.02000 |
| SO_4^{2-} (mg/L) | 250 | 0 | 0.00400 |
| F^- (mg/L) | 1.5 | 0 | 0.66667 |
| Fe (mg/L) | 0.3 | 0 | 3.33333 |
| As (mg/L) | 0.01 | 0 | 100 |

The presentation of the physio-chemical parameters selected in all the sampling sites and the corresponding WQI values are in a tabular form. Excellent, good, poor, very poor and unfit for human consumption were then used to proportion the groundwater quality of the estimated WQI values.

Table 4.11 WQI range, status and possible usage of the water sample (Brown et al., 1972)

| WQI | Water quality status (WQS) | Possible usage |
|-----------|--|--------------------------------------|
| 0-25 | Excellent | Drinking, irrigation and industrial |
| 26-50 | Good | Drinking, irrigation and industrial |
| 51-75 | Poor | Irrigation and industrial |
| 76-100 | Very poor | Irrigation |
| Above 100 | Unsuitable for drinking and fish culture | Proper treatment required before use |

It was observed that about 85.29% of the water sample fall under excellent, 11.76 % is under good and 2.94% is poor category. This implies that most of the groundwater at the study area are suitable for drinking and irrigation proposes. The 2.94% which were poor may be as result of various anthropogenic activities like lack of proper sanitation system, agricultural run-off, the inflow of direct sewerage from residential establishments, and unabated dumping of solid wastes by the community.

Table 4.12 Water quality index (WQI) classification for individual samples

| Community | ID | WQI | Description |
|---------------------------------------|-------|-------|-------------|
| Amutanga | KNW1 | 0.425 | Excellent |
| Saa-Agedi | KNW2 | 0.495 | Excellent |
| Saa-Agedi | KNW3 | 0.401 | Excellent |
| Baloo | KNW6 | 0.499 | Excellent |
| Mirigu Chips Compound | KNW14 | 0.405 | Excellent |
| Nakong Saboro | KNW20 | 0.315 | Excellent |
| Kalivio Gugoro | KNW23 | 1.021 | Excellent |
| Kalivio Gugoro | KNW24 | 0.569 | Excellent |
| Abulu | KNW26 | 0.349 | Excellent |
| Adongo | KNW29 | 0.359 | Excellent |
| Banyiu | KNW31 | 0.929 | Excellent |
| Wuru Chips Compound | KNW33 | 0.177 | Excellent |
| Kawanua | KNW34 | 0.503 | Excellent |
| Navem | KNW4 | 0.9 | Excellent |
| Navem | KNW5 | 0.305 | Excellent |
| Saka Chips Compound | KNW7 | 0.452 | Excellent |
| Chania Chips Compound | KNW8 | 0.455 | Excellent |
| Bugsongu | KNW9 | 30.46 | Good |
| Bugsongu JHS | KNW10 | 0.411 | Excellent |
| Kassena Nankana East Health Centre | KNW11 | 0.105 | Excellent |

| | | | |
|----------------------------------|-------|-------|-----------|
| Longo Chips Compound | KNW12 | 19 | Excellent |
| Mirigu Chips Compound | KNW13 | 0.448 | Excellent |
| Kandiga-Agandaa Primary SCH | KNW15 | 18.08 | Excellent |
| Navio E/H Prim | KNW16 | 0.134 | Excellent |
| Badunu | KNW17 | 0.545 | Excellent |
| Tedam JHS | KNW18 | 0.208 | Excellent |
| Nakong Chips Compound | KNW19 | 0.258 | Excellent |
| Saa Chips Compound | KNW21 | 0.375 | Excellent |
| Kalivio Gugoro Chips Compound | KNW22 | 58.64 | Poor |
| Abulu KG,Prim,JHS SCH | KNW25 | 0.368 | Excellent |
| Akania | KNW27 | 34.01 | Good |
| Akania | KNW28 | 0.384 | Excellent |
| Aneo (pump removed) | KNW30 | 0.835 | Excellent |
| Wuru Chips Compound | KNW32 | 0.16 | Excellent |

4.2.10 Stable Isotope (Oxygen-18 And Deuterium)

The Local Meteoric Water Line equation (LMWL) (Akiti, 1980) and the Global Meteoric Water Line (GMWL) (Coplen, 1996) were the two meteoric water line incorporated. The Local Meteoric Water Line (Akiti, 1980) is given as;

$$\delta^2\text{H} = 7.86\delta^{18}\text{O} + 13.61 \text{ and}$$

The Global Meteoric Water Line (GMWL) is given as;

$$\delta^2\text{H} = 8\delta^{18}\text{O} + 10$$

The LMWL (Akiti, 1980) was the suitable factor for the studies since the study area lies in the Upper region of Ghana and Akiti (1980) work was in the Accra plains in the South-Eastern part and Upper Regions of Ghana. The isotopic composition results of the groundwater in the study area were plotted on $\delta^{18}\text{O}$ vrs δD diagram.

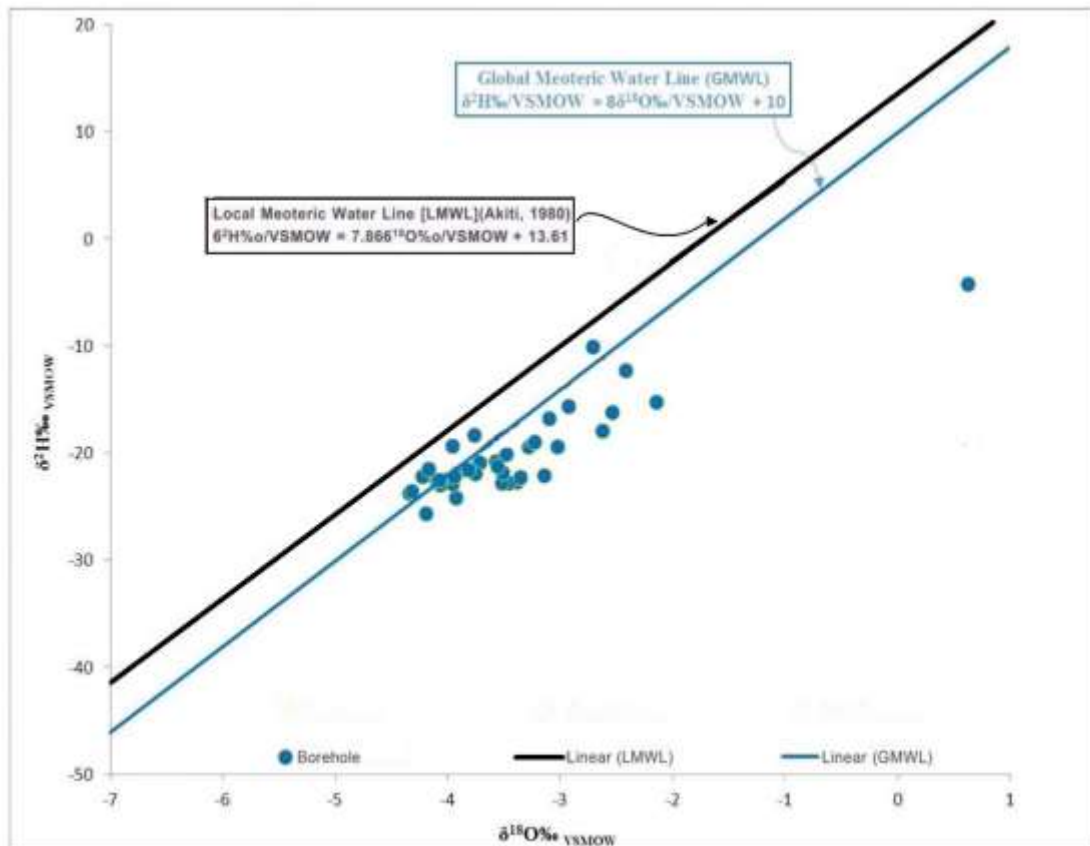


Figure 4.23: A plot $\delta^{18}\text{O} - \delta^2\text{H}$ showing relationships for isotopic composition of Akiti (1980) (LMWL), GMWL, groundwater .

4.2.11 Isotope composition of groundwater

The groundwater isotopic composition in the study area varies from -2.57 to -4.92‰ with mean isotopic content of -3.75 for $\delta^{18}\text{O}$ and from -14.86‰ to -29.15‰ with a mean isotopic composition of -20.20‰ for δD . Akiti (1980, 1982) reported comparable mean isotopic composition in Paga and Bolgatanga in the Upper east region of Ghana. The isotopic composition with the maximum value -2.57‰ and -14.86‰ $\delta^{18}\text{O}$ and δD respectively, suggested that the water have encountered a substantial evaporation before recharge and this may also imply the recharged is from an enriched source.

The revealing of the effects of high temperatures, low relative humidity, slow infiltration rates and high evaporation rates over the unsaturated zone is as a result of decrease in the evaporation line slope and deuterium excess than the GMWL.

Comparatively, the LMWL was higher than evaporation Line slope of the groundwater in the study area. This implies that, before recharge the infiltrating rainwater suffered some evaporation or there was distinct of evaporation of raindrops. The LMWL and SWL lines intersect at a point where $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are, respectively, -26‰ and -5‰. This is the sign of the rainwater that recharged the groundwater (Akiti, 1980).

However, the direct groundwater recharge from precipitation depends on the thickness and nature of the overburden material and the dominant weather conditions that directs the portion of rainfall that moves into the saturated zone (Yidana, 2013).

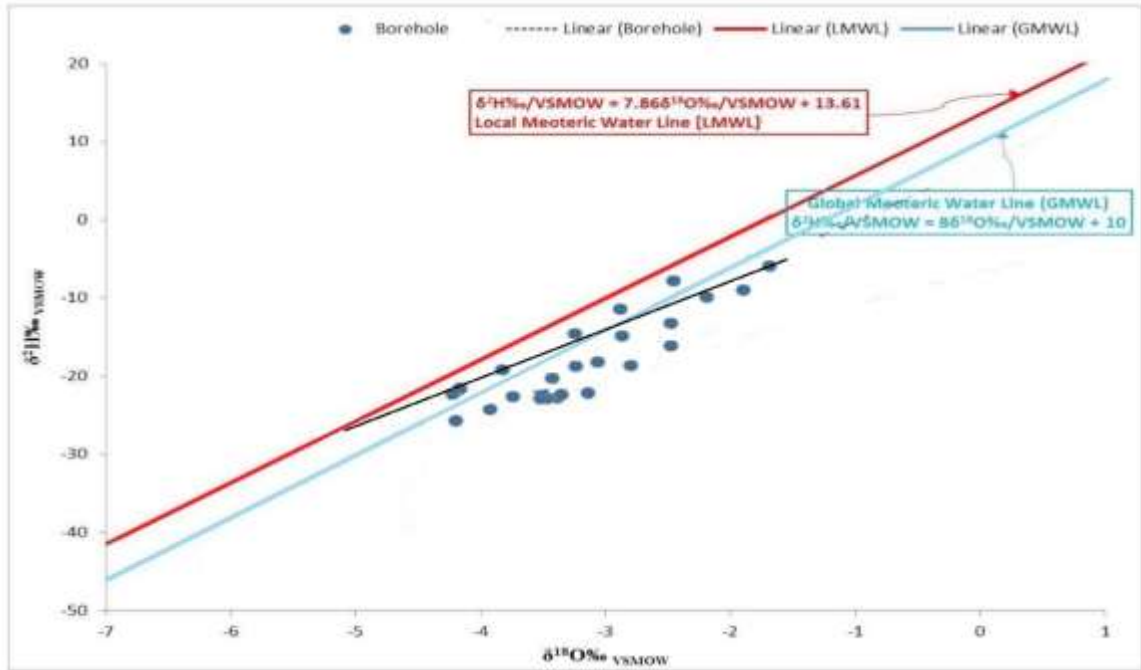


Figure 4.24: Relationship between the LMWL, GMWL and BWL in the study area.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1.1 Bongo District

This chapter delineates the main conclusions of the study carried out with the main objective of using hydrochemical and isotopic tracers to assess the impact of anthropogenic activities on groundwater quality in Bongo and Kassena Nankana West Districts in Upper East Region of Ghana, due to intensive farming activities by the people and increasing population.

The hydrogeochemical analysis of the study discloses that the groundwater is near neutral to slightly alkaline and are fresh water. The order of the abundance of the major cation is $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ and anion is Cl^- , HCO_3^- , NO_3^- and SO_4^- , respectively. Na and Cl are dominant ions among the studied cations and anions, respectively. The concentrations of all the ions are within the permissible limit for drinking purpose except few locations which showed degree of deteriorating. About 6.66 % of the groundwater samples have exceeded the permissible limit of NO_3^- and 53% for F^-

According to Gibbs diagram, the predominant samples fall in the rock–water interaction dominance. The piper trilinear diagram shows that groundwater in the study area is Ca-Na+K- Cl and mixed Cl+SO₄- HCO₃ and Na-Ca-Mg types. The Hierarchical Cluster Analysis (HCA) further classified the groundwaters of the study area into two groups which show clear geo-hydrological patterns and different degrees of water-rock interaction or

mineralisation. Based on the WQI classification, majority of the samples are falling under excellent to good water category and suitable for drinking water purposes.

The stable isotopes composition quantities for groundwater of the study area clustered closely along the global meteoric water line (GMWL), signifying an integrative recharge from meteoric origin. Nevertheless, few groundwater samples, clustered below the global meteoric water line (GMWL) display they was distinct evaporation before recharge.

5.1.2 Kassena Nankana

The hydrogeochemical analysis of Kassena Nankana West District show that the groundwater is near neutral to slightly alkaline and are fresh water except study area KNW27 which recorded TDS value higher than the recommended limit. The order of the abundance of the major cation is $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and anion is $\text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{SO}_4^-$. Na and HCO_3^- are dominant ions among the studied cations and anions, respectively. The concentrations of all the ions are within the permissible limit for drinking purpose except few locations which showed degrees of deteriorating. About 8.8 %, 2.94 % and 17 % of the groundwater samples have exceeded the permissible limit of NO_3^- , Na^+ , Cl and F^- , respectively.

According to Gibbs diagram, the predominant samples fall in the rock–water interaction dominance. The piper trilinear diagram shows that groundwater in the study area is Ca-Na+K, HCO_3^- -Cl and Cl+ SO_4^- - HCO_3^- mixed type. The Hierarchical Cluster Analysis (HCA) further classified the groundwaters of the study area into two groups which show clear geo-hydrological patterns and different degrees of water-rock interaction or mineralization.

Based on the WQI classification, majority of the samples are falling under excellent to good water category and suitable for drinking water purposes.

The stable isotopes composition quantities for groundwater of the study area clustered closely along the global meteoric water line (GMWL), signifying an integrative recharge from meteoric origin. Nevertheless, few groundwater samples, clustered below the global meteoric water line (GMWL) display that, there was distinct evaporation before recharge .

5.1.3 General Conclusions from Bongo and Kassena Nankana West Districts

In general, majorities of the ions are within the permissible limit for drinking purpose except few locations for both study areas which showed degrees of deteriorating.

The Gibbs diagram, the piper trilinear diagram and the Hierarchical Cluster Analysis reveal different degrees of water-rock interaction or mineralisation. Based on the WQI classification majority of the samples are falling under excellent to good water category and suitable for drinking water purposes.

The stable isotopes composition implies, before groundwater recharge, the groundwater have been subjected to evaporation either in the surface before recharge or in the unsaturated zone or those which stayed longer in the surface and polluted before recharge.

5.2 Recommendations

The human population living in the Bongo and Kassena Nankana West Districts depend on groundwater to expand upon their socio-economic livelihood; therefore, the following are recommended:

- i) The present surface water do not reach the groundwater immediately and that if the previous one carried some contaminants; it may take long time to reach the groundwater due to; the thickness of the unsaturated zone of the study areas and the unsaturated zone that lies immediately above the aquifer is not saturated. Hence, thorough geochemical study in the unsaturated zone should be encouraged in both study areas
- ii) Although the study showed that majorities of groundwater were of excellent chemical quality, it is recommended that good agricultural practices and good sanitation should be encouraged in order to protect the groundwater from pollution.
- iii) Finally, groundwater in and around Mirigu, Akania, Kassena Nakanna West Health Center, Tarongo, Aberingabisi, Naveem, Kalivio CHPS compound, Aneo, Kalivio Gugoro, Banyui, Sambolo Basic School, Atampiisi CHPS Compound, Bongo Senior High School, St. Ann Primary School and Anafobisi Zuen communities should be monitored since they showed deteriorating water quality.

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APPENDIXES

Appendix A. 1: Physio-chemical, chemical (mg/L) and isotopic composition (δ ‰VSMOW) of ground water in Bongo

| ID | pH | EC | TDS | Sal | Temp | HCO ₃ ⁻ | Ca | Mg | Na | K | F ⁻ | Cl ⁻ | NO ₃ ⁻ | PO ₄ ³⁻ | SO ₄ ²⁻ | $\delta^{18}\text{O}$ | $\delta^2\text{H}$ | Fe | Mn | As |
|------|------|-------|------|------|-------|-------------------------------|------|------|-------|------|----------------|-----------------|------------------------------|-------------------------------|-------------------------------|-----------------------|--------------------|--------|--------|--------|
| | | uS/cm | mg/l | ppt | oC | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l | ‰ | ‰ | mg/l | mg/l | mg/l |
| BG2 | 6.35 | 354 | 195 | 0.10 | 32.30 | 48.00 | 20.8 | 1.20 | 51.40 | 4.90 | 1.32 | 68.03 | 7.93 | 0.07 | 8.13 | -3.99 | -19.39 | <0.006 | <0.002 | <0.001 |
| BG3 | 6.06 | 225 | 124 | 0.00 | | 28.00 | 9.6 | 0.61 | 28.30 | 2.78 | 1.08 | 45.09 | 6.09 | 0.10 | 8.70 | -4.26 | -20.52 | <0.006 | <0.002 | <0.001 |
| BG4 | 6.66 | 301 | 165 | 0.10 | 31.70 | 52.00 | 11.2 | 1.10 | 39.10 | 2.58 | 1.29 | 42.99 | 12.25 | 0.06 | 8.99 | -3.62 | -18.41 | <0.006 | 0.017 | <0.001 |
| BG6 | 6.57 | 372 | 204 | 0.10 | 32.50 | 76.00 | 19.2 | 1.15 | 65.20 | 2.34 | 1.97 | 83.51 | 2.15 | 0.17 | 5.37 | -3.61 | -21.56 | <0.006 | <0.002 | <0.001 |
| BG7 | 6.70 | 389 | 214 | 0.10 | 32.90 | 60.00 | 32.4 | 1.23 | 56.30 | 2.49 | 1.43 | 89.08 | 5.01 | 0.06 | 2.99 | -3.79 | -20.09 | <0.006 | <0.002 | <0.001 |
| BG11 | 6.56 | 409 | 225 | 0.10 | 31.90 | 64.00 | 32 | 1.18 | 50.70 | 0.80 | 0.54 | 79.79 | 4.74 | 0.04 | 3.97 | -3.91 | -22.38 | <0.006 | <0.002 | <0.001 |
| BG16 | 6.59 | 521 | 287 | 0.20 | 31.90 | 116.00 | 25.6 | 1.33 | 86.80 | 7.10 | 0.88 | 142.3 | 9.50 | 0.26 | 2.11 | -4.40 | -23.10 | <0.006 | <0.002 | <0.001 |
| BG17 | 6.45 | 251 | 138 | 0.00 | 31.60 | 36.00 | 14.4 | 1.11 | 35.90 | 5.00 | 0.55 | 69.19 | 9.97 | 0.06 | 2.06 | -3.86 | -21.33 | 0.1535 | <0.002 | <0.001 |
| BG20 | 6.53 | 421 | 232 | 0.10 | 31.70 | 52.00 | 24 | 1.30 | 59.50 | 2.36 | 1.96 | 91.07 | 8.97 | 0.70 | 1.84 | -3.60 | -19.15 | <0.006 | <0.002 | <0.001 |
| BG26 | 6.77 | 372 | 204 | 0.10 | 30.70 | 44.00 | 28.8 | 1.18 | 50.50 | 7.60 | 1.98 | 94.74 | 8.09 | 0.16 | 1.74 | -3.64 | -20.83 | 0.1195 | 0.0095 | <0.001 |
| BG28 | 6.81 | 293 | 161 | 0.10 | 31.50 | 60.00 | 14.4 | 1.20 | 38.80 | 5.20 | 1.37 | 61.01 | 5.07 | 0.22 | 0.06 | -3.98 | -21.73 | 0.086 | <0.002 | <0.001 |
| BG1 | 6.35 | 354 | 195 | 0.10 | 32.30 | 48.00 | 6.4 | 0.59 | 75.80 | 1.20 | 1.26 | 87.00 | 4.01 | 0.61 | 6.53 | -4.22 | -21.54 | 0.054 | 0.0175 | <0.001 |
| BG5 | 6.76 | 293 | 161 | 0.10 | 32.40 | 44.00 | 19.2 | 1.23 | 29.10 | 1.20 | 1.02 | 61.13 | 5.01 | 0.09 | 5.97 | -3.74 | -15.81 | 0.128 | <0.002 | 0.003 |
| BG8 | 7.17 | 442 | 243 | 0.10 | 32.80 | 84.00 | 35.2 | 1.32 | 46.10 | 2.77 | 3.74 | 62.27 | 10.16 | 0.06 | 8.04 | -3.82 | -20.00 | 0.3655 | 0.0015 | 0.002 |
| BG9 | 6.65 | 389 | 214 | 0.10 | 32.60 | 76.00 | 16 | 0.99 | 62.50 | 2.70 | 3.46 | 91.37 | 4.52 | 0.01 | 5.01 | -3.07 | -18.26 | 0.3685 | <0.002 | 0.002 |
| BG10 | 6.98 | 608 | 334 | 0.20 | 32.20 | 126.40 | 35.2 | 1.26 | 66.40 | 0.50 | 0.68 | 108.38 | 5.60 | 0.05 | 6.93 | -3.35 | -16.93 | <0.006 | <0.002 | <0.001 |

| | | | | | | | | | | | | | | | | | | | | |
|------|------|-------|-----|------|-------|--------|------|------|-------|------|------|--------|------|------|-------|-------|--------|--------|--------|--------|
| BG12 | 6.87 | 298 | 164 | 0.10 | 33.50 | 64.00 | 25.6 | 1.15 | 49.60 | 5.89 | 0.71 | 81.95 | 4.87 | 0.30 | 2.64 | -4.36 | -19.57 | <0.006 | <0.002 | <0.001 |
| BG13 | 7.13 | 459 | 252 | 0.10 | 32.70 | 76.00 | 41.6 | 1.14 | 51.70 | 1.78 | 1.07 | 80.55 | 7.48 | 0.18 | 4.86 | -2.62 | -14.98 | <0.006 | <0.002 | <0.001 |
| BG14 | 6.57 | 292 | 161 | 0.10 | 32.80 | 64.00 | 20.8 | 0.63 | 41.90 | 0.60 | 0.98 | 78.09 | 2.66 | 0.08 | 0.01 | -4.52 | -22.48 | 0.3035 | <0.002 | 0.0015 |
| BG15 | 6.38 | 171.5 | 94 | 0.00 | 32.00 | 32.00 | 9.6 | 1.23 | 17.90 | 4.20 | 0.29 | 28.83 | 3.50 | 0.12 | 1.65 | -3.60 | -18.78 | <0.006 | <0.002 | <0.001 |
| BG18 | 6.90 | 524 | 288 | 0.20 | 32.70 | 108.00 | 30.4 | 1.30 | 45.90 | 8.71 | 0.87 | 91.80 | 4.89 | 0.97 | 1.03 | -3.94 | -22.18 | <0.006 | <0.002 | <0.001 |
| BG19 | 6.82 | 567 | 312 | 0.20 | 32.00 | 132.00 | 41.6 | 1.33 | 61.30 | 6.21 | 0.73 | 133.56 | 4.32 | 0.60 | 0.64 | -3.86 | -19.64 | <0.006 | <0.002 | <0.001 |
| BG21 | 6.80 | 262 | 144 | 0.00 | 32.00 | 60.00 | 20.8 | 1.09 | 34.60 | 3.65 | 0.84 | 43.02 | 3.10 | 0.05 | 1.85 | -3.48 | -15.83 | <0.006 | <0.002 | <0.001 |
| BG22 | 6.80 | 274 | 151 | 0.00 | 31.40 | 44.00 | 19.2 | 1.01 | 44.30 | 1.57 | 0.97 | 61.95 | 2.05 | 0.72 | 1.07 | -3.62 | -18.99 | <0.006 | <0.002 | <0.001 |
| BG23 | 6.78 | 405 | 223 | 0.10 | 31.60 | 68.00 | 28.8 | 1.25 | 47.20 | 4.57 | 2.34 | 99.42 | 1.57 | 0.09 | 0.74 | -3.48 | -19.64 | 0.024 | <0.002 | <0.001 |
| BG24 | 6.65 | 511 | 281 | 0.00 | 32.10 | 60.00 | 38.4 | 1.23 | 53.70 | 5.60 | 2.62 | 142.19 | 0.33 | 0.10 | 2.98 | -3.69 | -18.43 | 0.128 | <0.002 | 0.006 |
| BG25 | 7.09 | 708 | 389 | 0.30 | 31.10 | 69.00 | 60.8 | 1.08 | 75.80 | 3.70 | 2.79 | 169.59 | 8.50 | 0.22 | 11.00 | -4.05 | -21.34 | <0.006 | <0.002 | <0.001 |
| BG27 | 7.02 | 348 | 192 | 0.10 | 32.90 | 72.00 | 24 | 1.18 | 41.90 | 2.10 | 1.02 | 78.25 | 4.02 | 1.10 | 2.41 | -3.90 | -21.90 | 0.201 | 0.0095 | <0.001 |
| BG29 | 6.25 | 115.4 | 63 | 0.00 | 30.80 | 24.00 | 8 | 0.60 | 12.60 | 8.00 | 0.90 | 22.01 | 1.08 | 0.07 | 1.67 | -3.93 | -20.25 | 0.104 | 0.0055 | <0.001 |
| BG30 | 6.79 | 284 | 156 | 0.00 | 32.50 | 60.00 | 19.2 | 1.22 | 32.30 | 3.78 | 0.97 | 50.08 | 6.33 | 1.01 | 2.68 | -4.40 | -24.00 | <0.006 | <0.002 | <0.001 |

Appendix A. 2: Physio-chemical, chemical (mg/L) and isotopic composition (δ ‰VSMOW) of ground water in kassena Nankana.

| ID | EC | pH | TDS | Sal | Temp | HCO ₃ ⁻ | Ca | Mg | Na | K | F ⁻ | Cl ⁻ | NO ₃ ⁻ | PO ₄ ³⁻ | SO ₄ ²⁻ | $\delta^{18}\text{O}$ | $\delta^2\text{H}$ | Fe | Mn | As |
|-------|-------|------|------|------|-------|-------------------------------|------|------|--------|------|----------------|-----------------|------------------------------|-------------------------------|-------------------------------|-----------------------|--------------------|--------|--------|--------|
| | uS/cm | | mg/l | Ppt | °C | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l | ‰ | ‰ | mg/l | mg/l | mg/l |
| KNW1 | 479 | 6.89 | 264 | 0.20 | 31.70 | 88.00 | 21.8 | 1.18 | 61.70 | 1.08 | 0.97 | 69.44 | 8.52 | 1.92 | 0.13 | -3.81 | -21.22 | <0.006 | <0.002 | <0.001 |
| KNW2 | 463 | 7.07 | 255 | 0.10 | 33.30 | 104.00 | 28.8 | 1.30 | 42.30 | 2.01 | 1.10 | 46.27 | 9.99 | 0.09 | 1.04 | -3.08 | -18.11 | <0.006 | <0.002 | <0.001 |
| KNW3 | 407 | 7.74 | 224 | 0.10 | 33.90 | 100.00 | 23 | 1.22 | 41.30 | 1.27 | 0.77 | 39.86 | 5.10 | 0.51 | 0.94 | -3.96 | -19.23 | <0.006 | 0.0145 | <0.001 |
| KNW6 | 314 | 6.90 | 173 | 0.10 | 32.80 | 60.00 | 10.4 | 1.19 | 44.90 | 0.48 | 1.16 | 34.10 | 9.54 | 0.06 | 4.11 | -3.51 | -20.71 | <0.006 | <0.002 | <0.001 |
| KNW14 | 794 | 7.92 | 437 | 0.30 | 31.20 | 112.00 | 38.4 | 1.28 | 113.00 | 2.91 | 0.71 | 124.22 | 28.73 | 0.07 | 2.10 | -3.28 | -17.37 | <0.006 | <0.002 | <0.001 |
| KNW20 | 414 | 6.05 | 228 | 0.10 | 32.00 | 88.00 | 19.2 | 1.25 | 47.50 | 1.10 | 0.87 | 58.10 | 3.08 | 0.01 | 4.97 | -3.77 | -18.47 | 0.029 | <0.002 | <0.001 |
| KNW23 | 419 | 6.95 | 231 | 0.10 | 31.40 | 92.00 | 8.4 | 1.09 | 61.00 | 6.22 | 2.37 | 56.07 | 3.37 | 0.16 | 0.01 | -3.94 | -20.98 | 0.07 | <0.002 | <0.001 |
| KNW24 | 513 | 6.83 | 282 | 0.20 | 31.30 | 92.00 | 18.4 | 0.59 | 55.3 | 2.60 | 1.33 | 54.09 | 2.42 | 0.41 | 2.62 | -3.94 | -19.83 | 0.038 | <0.002 | <0.001 |
| KNW26 | 510 | 6.36 | 281 | 0.20 | 33.00 | 80.00 | 22 | 1.23 | 44.50 | 4.94 | 0.89 | 56.09 | 8.65 | 1.18 | 1.33 | -3.55 | -19.44 | 0.0405 | <0.002 | <0.001 |
| KNW29 | 321 | 6.70 | 177 | 0.10 | 31.30 | 63.89 | 14.4 | 1.07 | 36.60 | 0.60 | 0.87 | 41.07 | 2.14 | 0.07 | 4.06 | -3.64 | -18.76 | 0.133 | 0.0015 | <0.001 |
| KNW31 | 528 | 6.94 | 291 | 0.20 | 34.60 | 100.00 | 10.4 | 1.13 | 56.20 | 4.87 | 2.15 | 67.76 | 3.98 | 1.19 | 5.23 | -4.08 | -20.59 | 0.08 | 0.0145 | <0.001 |
| KNW33 | 458 | 6.50 | 252 | 0.10 | 31.90 | 96.00 | 38.4 | 1.28 | 46.80 | 3.25 | 0.46 | 87.14 | 1.00 | 0.05 | 1.97 | -3.86 | -21.51 | 0.0305 | <0.002 | <0.001 |
| KNW34 | 343 | 6.74 | 189 | 0.10 | 31.70 | 72.00 | 17.2 | 1.32 | 39.90 | 0.87 | 1.20 | 42.87 | 2.06 | 0.68 | 6.00 | -3.56 | -19.08 | 0.174 | 0.018 | <0.001 |
| KNW4 | 318 | 6.89 | 175 | 0.10 | 33.50 | 60.00 | 14 | 1.13 | 48.00 | 1.80 | 2.10 | 45.19 | 9.81 | 0.06 | 2.08 | -3.64 | -18.08 | <0.006 | 0.002 | <0.001 |
| KNW5 | 831 | 6.73 | 457 | 0.10 | 32.00 | 68.00 | 65.6 | 1.33 | 104.00 | 2.20 | 0.70 | 217.72 | 6.51 | 0.20 | 2.01 | -2.9 | -16.92 | <0.006 | <0.002 | <0.001 |
| KNW7 | 487 | 7.30 | 286 | 0.20 | 32.50 | 100.00 | 32 | 1.04 | 48.00 | 4.54 | 0.96 | 52.61 | 8.39 | 0.01 | 1.75 | -3.73 | -21.1 | <0.006 | <0.002 | <0.001 |
| KNW8 | 696 | 6.60 | 383 | 0.30 | 31.20 | 88.00 | 44.8 | 1.31 | 96.60 | 5.90 | 1.08 | 163.10 | 8.48 | 1.28 | 6.85 | -3.87 | -20.75 | <0.006 | <0.002 | <0.001 |
| KNW9 | 449 | 7.09 | 247 | 0.10 | 33.10 | 104.00 | 28.8 | 1.16 | 60.20 | 0.20 | 0.38 | 65.05 | 6.91 | 0.02 | 1.19 | -3.77 | -19.86 | 0.5875 | 0.0145 | 0.0025 |

| | | | | | | | | | | | | | | | | | | | | |
|-------|------|------|-----|------|-------|--------|------|------|--------|-------|------|--------|-------|------|------|-------|--------|--------|---------|--------|
| KNW10 | 469 | 7.13 | 258 | 0.10 | 33.90 | 108.00 | 32.2 | 1.20 | 62.10 | 0.52 | 0.89 | 62.06 | 7.01 | 0.09 | 2.08 | -3.58 | -18.28 | <0.006 | 0.0015 | <0.001 |
| KNW11 | 616 | 7.44 | 338 | 0.20 | 33.40 | 116.00 | 32 | 1.28 | 74.40 | 4.33 | 0.11 | 121.76 | 10.69 | 0.03 | 1.07 | -3.57 | -20.17 | <0.006 | <0.002 | <0.001 |
| KNW12 | 487 | 7.14 | 268 | 0.20 | 32.40 | 108.00 | 40 | 1.30 | 54.40 | 1.20 | 0.84 | 67.73 | 9.61 | 0.03 | 3.01 | -2.57 | -14.86 | 0.881 | 0.02425 | 0.001 |
| KNW13 | 617 | 7.79 | 339 | 0.20 | 31.30 | 80.00 | 44.8 | 1.24 | 74.90 | 0.50 | 0.85 | 160.11 | 14.30 | 1.10 | 1.23 | -3.29 | -18.15 | 0.2485 | 0.0335 | <0.001 |
| KNW15 | 366 | 6.32 | 201 | 0.10 | 31.60 | 60.00 | 30.6 | 1.31 | 30.40 | 0.80 | 0.95 | 47.05 | 8.56 | 0.28 | 3.00 | -3.95 | -22.2 | 0.3105 | 0.005 | 0.0015 |
| KNW16 | 261 | 6.32 | 144 | 0.20 | 35.10 | 32.00 | 16.8 | 1.28 | 33.00 | 4.10 | 0.41 | 51.10 | 4.03 | 1.49 | 2.87 | -4.22 | -25.82 | <0.006 | <0.002 | <0.001 |
| KNW17 | 310 | 6.27 | 171 | 0.10 | 33.70 | 64.00 | 30.4 | 0.63 | 39.70 | 0.30 | 1.37 | 61.98 | 2.37 | 0.01 | 1.96 | -4.33 | -21.97 | 0.031 | 0.0065 | <0.001 |
| KNW18 | 472 | 6.38 | 260 | 0.20 | 31.60 | 88.00 | 27.2 | 1.07 | 42.50 | 1.00 | 0.56 | 39.95 | 3.07 | 1.01 | 4.92 | -4.13 | -22.24 | 0.3471 | 0.236 | <0.001 |
| KNW19 | 309 | 6.66 | 170 | 0.10 | 32.40 | 68.00 | 32 | 1.39 | 23.60 | 2.67 | 0.63 | 39.87 | 2.96 | 0.10 | 6.02 | -3.85 | -19.14 | 0.802 | 0.03 | <0.001 |
| KNW21 | 687 | 6.85 | 378 | 0.30 | 34.70 | 112.00 | 32 | 1.29 | 81.60 | 16.10 | 0.85 | 147.20 | 7.26 | 0.06 | 2.75 | -3.42 | -19.17 | 0.0375 | <0.002 | <0.001 |
| KNW22 | 427 | 7.03 | 236 | 0.10 | 31.00 | 100.00 | 24 | 1.34 | 68.00 | 1.30 | 3.70 | 64.07 | 4.25 | 0.68 | 2.19 | -4.05 | -20.32 | 0.3979 | 0.0615 | 0.0055 |
| KNW25 | 455 | 6.14 | 249 | 0.10 | 32.00 | 88.00 | 28.8 | 1.26 | 50.40 | 0.80 | 0.97 | 71.86 | 6.36 | 1.00 | 3.90 | -4.07 | -19.69 | 0.33 | 0.0095 | <0.001 |
| KNW27 | 1074 | 6.66 | 590 | 0.50 | 31.80 | 128.00 | 21.2 | 1.22 | 215.90 | 2.68 | 4.27 | 298.87 | 9.54 | 3.38 | 5.38 | -3.51 | -19.5 | 0.3172 | 0.2405 | 0.003 |
| KNW28 | 469 | 7.03 | 257 | 0.10 | 31.60 | 84.00 | 22.4 | 1.37 | 61.00 | 8.33 | 0.86 | 87.10 | 2.20 | 0.19 | 1.52 | -4.92 | -29.15 | 0.1295 | 0.018 | <0.001 |
| KNW30 | 571 | 7.07 | 314 | 0.20 | 31.10 | 120.00 | 40 | 0.69 | 94.50 | 0.62 | 1.89 | 161.07 | 4.44 | 0.99 | 5.06 | -4.33 | -23.32 | 0.169 | 0.009 | <0.001 |
| KNW32 | 395 | 6.45 | 217 | 0.10 | 31.60 | 76.00 | 38.4 | 1.24 | 42.20 | 0.80 | 0.43 | 66.93 | 5.10 | 0.07 | 4.87 | -3.7 | -20.76 | 0.0535 | <0.002 | <0.001 |

EC (Electrical conductivity), **TDS** (Total Dissolved Solid), **Temp** (Temperature), **Sal** (Salinity)

