HYDROGEOCHEMICAL AND ISOTOPIC STUDIES OF GROUND AND SURFACE WATERS IN THE LOWER ANAYARI CATCHMENT AREA, UPPER EAST REGION OF GHANA

THIS THESIS IS SUBMITTED TO THE UNIVERSITY OF GHANA, LEGON IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF MPHIL NUCLEAR AND RADIOCHEMISTRY DEGREE

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DECLARATION

This is to certify that this thesis is the result of research work undertaken by **Dickson Abdul-Wahab** towards the Degree of M.Phil. Nuclear and Radiochemistry in the Department of Nuclear Science and Applications, School of Nuclear and Allied Science (SNAS), University of Ghana, Legon, under the supervision of **Prof. Dickson Adomako** and **Dr. Dennis K. Adotey**.

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ABSTRACT

The Lower Anayari catchment (LAC) located in the Upper East Region of Ghana, is part of the transboundary (Ghana and Burkina Faso) Anayari catchment. The other transboundary catchments are Atankwidi and Yarigatanga. These catchments are noted for intense farming activities. The population within Lower Anayari catchment area is estimated to be about 19,445. An estimate of about 80% of the population depends on groundwater for domestic and agricultural purposes. Agriculture has direct or indirect effects on the chemical composition of groundwater and aquifer geochemistry. This study was carried out to investigate the dominant geochemical processes and anthropogenic activities that influence groundwater chemistry in LAC. The study employed hydrochemistry and isotopic techniques to assess the chemical quality of groundwater in the Lower Anayari catchment. A total of fifty-one (51) samples comprising of thirty-seven (37) boreholes, four (4) hand-dug well and ten (10) surface waters were sampled from six (6) principal communities (Kulwase, Manyoro, Mirigu, Nakolo, Paga and Pungu) 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^+ (Flame photometry), Ca^{2+} (complexometric titration), and F^-, Cl^-, NO_3^-, PO_4^{3-}, and SO_4^{2-} (ion chromatography). Atomic absorption spectrometry was used for the determination of Mg^{2+} and heavy metals (Fe, Co, Cd, As, Ni, and Pb). 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]. The general trend of major cations and anions, and trace element concentration were $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$, $HCO_3^- > Cl^- > NO_3^- > SO_4^{2-}$, and Fe > Pb > As > Co > Cd > Ni respectively. The concentration of Ni [0.001 - 0.019], As [0.001 - 0.008], Co [0.005 - 0.010], and Fe [0.006 - 0.586] mg/L, were averagely below WHO standard values for drinking water. The concentration of Cd [0.002 - 0.006] and Pb [0.001 - 0.020] mg/L, were averagely above WHO standard values (0.003 and 0.01 mg/L respectively) for drinking water. The data was subjected to Principal Component Analysis (PCA) this help delineate principal physico-chemical processes (related to minerals dissolutions, organic and synthetic fertilizers influences) implicated in groundwater quality. Hierarchical Cluster Analysis (HCA) further classified the groundwaters of the study area into two groups. The groups show different degrees of water-rock interaction or mineralisation. Water Quality Index (WQI) estimations indicated that the groundwater in the study area is suitable for drinking with the exception of groundwater in Nakolo and Mirigu which showed deteriorating water quality. Piper Trilinear plot indicated three (3) hydrochemical facies Ca-Mg-HCO_3, Na-Ca-HCO_3 and Na-HCO_3 and are consequence of silicate weathering and silicate mineral dissolution, cation exchange and to a lesser extent fertilizer application which is more evident in Nakolo and Mirigu communities. The Wilcox diagram, and the United States Salinity Laboratory diagram (USSL) method for assessment of the groundwater suitability for irrigation revealed that the groundwater from the LAC are suitable for irrigation. Stable isotopes composition measurements for groundwater River Anayari and irrigation dams were clustered closely along the global meteoric water line (GMWL) suggesting an integrative recharge from meteoric origin, with a few showing evaporation effects before recharge.

Dedicated

To my Mum and Dad

Madam Gifty Quaye and Mr. Yakubu Dickson

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AHC	Agglomerative Hierarchical Clustering
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
IDW	Inverse Distance Weighted Interpolation
IDWL	Irrigation Dam Water Evaporation Line
LAC	Lower Anayari Catchment
LMWL	Local Meteoric Water Line
PCA	Principal Component Analysis
PCB	Precambrian Basement
RSC	Residual Sodium Carbonate
RWL	River Water Evaporation Line
SAR	Sodium Adsorption Ratio
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

CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND

Freshwater is a necessity for life, and a very important natural resource of the ecological system. The availability of freshwater resources plays a key role in promoting good living standards, enhancing economic growth, food security and livelihood, and eventually alleviating poverty (Adomako, 2010). Freshwater constitutes less than 3% of the world's water resources (Odada, 2006). River, streams , lakes and groundwater available and usable for the ecosystem and humans constitute 1% of world's 3% of freshwater (IAEA, 2011). Surface waters (rivers, streams and lakes) are easily susceptible to pollution. Pollution of surface water is the major cause of water-borne and water-related diseases such as, guinea worm infestation, bilharzias, and typhoid fever (Alleyne et al., 2015; Vellinga, 2015). According to the IAEA (2011), groundwater constitutes one-third of global freshwater available for use. Groundwater is much less susceptible to pollution, for much of it is in seclusion (WHO, 1993).

In Ghana, groundwater is one of the most important sources of water for domestic and household chores, irrigation and industrial use. This is probably because it is hardly contaminated thus require less or no chemical treatment before use, it is convenient for scattered settlements, so reduce relatively large cost involved in supplying treated water over long distances to serve communities, and lastly, is accessible even during extreme dry seasons. Clearly groundwater is a key freshwater resource for both rural and urban population, hence its assessment estimation, proper management and sustainability is a major concern (Adomako et al., 2010).

In the Upper East Region of Ghana, groundwater is a major source of freshwater for domestic purposes, agriculture and commercial 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). Additionally, short rainfall seasons, and long dry seasons, makes communities to often times experience inadequate benefits of surface water, hence, resort to the use of groundwater (Ofosu, 2011).

Therefore, provision of groundwater for communities has resulted in borehole drilling activities growing appreciably in the Upper East Region, mostly funded through development aid (Martin, 2006).

The Lower Anayari catchment is one of the trans-boundary neighbouring catchment areas (others are Atankwidi, Yarigatanga) noted for intense farming activities in Upper East Region. The population within Lower Anayari catchment area is estimated to be about 19,445 per the 2010 census (GSS, 2013). The major occupation of majority of the population is rain-fed farming, alongside animal rearing, petty trade and traditional cloth weaving. The main agricultural crops cultivated include millet, groundnut, rice, sorghum, cowpea, vegetables (tomatoes, pepper) and maize.

Apart from rain-fed agricultural practices, some of the farmers' practice irrigation farming using irrigation ponds whiles a very small fraction of farmers also practice irrigation farming along river banks using groundwater from dug-out wells during the dry season. As at 2010, irrigated lands covered an area of about 0.4 and 4.83 km^2 for government and private led irrigation schemes respectively (Ofosu, 2011). This is higher than in the two neighbouring catchment area namely; Atankwidi, Yarigatanga. The main irrigated crops are tomatoes, pepper, cabbage, and carrot. Field survey reveals that majority of the farmers apply manure on their farms while some vegetables and rice farmers apply inorganic fertilizers.

Studies have shown that frequent use of fertilizers by farmers can influence the chemical quality of groundwater. For instance, nitrate levels in groundwater measured in 1977 and 1980 in the Upper Region although they were low, shown a significant increase between 1977 to 1980, this was due to frequent use of fertilizers by farmers in the area (Akiti, 1982).

Groundwater use in the Lower Anayari Catchment is mainly for domestic purposes (such as drinking, cooking, washing, and for building and repair of mud houses), and agricultural purposes (such as watering of livestock and irrigation which seems minimal).

There is limited or scare data on the impact of agricultural activities on the groundwater system in the Lower Anayari catchment, and the availability of harmonised information and data will aid hydrogeologists to understand hydro-geochemical processes, which controls the water chemistry and the vulnerability of the aquifer to contamination within the Lower Anayari catchment.

In this study, multivariate statistical tools, bivariate plots and Piper diagram will be used to understand the chemical processes and to demonstrate possible evolution of a water-type into another groundwater type due to anthropogenic influences in the catchment based on hydrochemical data generated from the study. Furthermore, environmental isotopes of groundwater will be used as an additional tool to understand process and local process like selective infiltration, direct percolation and evaporation effect on the groundwater and possible interaction of surface water with groundwater in the catchment.

1.2 STATEMENT OF THE PROBLEM

In the Upper East Region, groundwater is significantly depend upon by communities as source of portable water (Martin, 2006). It is estimated that at least about 70% of people living in the Upper East region use groundwater as a source of drinking water, and in the dry season, fairly used for irrigation purposes (Adetunde and Glover, 2010; Ofosu et al., 2010; Ofosu, 2011; Oyelude et al., 2013).

Anthropogenic activities such as agricultural practices (fertilizers application) can pose a serious threat to the groundwater (British Geological Survey, 2009). Agriculture is the predominant land use within the Lower Anayari catchment of Upper East Region (Anayah and Kaluarachchi, 2009). Hence, intense farming activities are done during raining season, and crops cultivated include maize, millet, rice, guinea corn, and groundnuts.

The intensity of the farming activities is such that approximately every household farms, and farm areas are mostly located close to their houses, boreholes and other sources of water (small irrigation ponds/dams, dugout wells). Application of fertilizers are done mostly by rice, maize and vegetables farmers to increase productivity both in dry and rain season (Laary, 2012).

Groundwater occurrence in the study area are mainly controlled by secondary porosity as a result of chemical weathering, faulting and fracturing (SNC-Lavalin, 2011). Hence, wells and borehole sited are in fractured or sheared zone, resulting in high probability of easy gravitational movement of water into aquifer (Akiti, 1982). The groundwater table in the weathered zone of the study area range between 5 m to 30 m (Martin, 2006).

Therefore, the probability of contaminants like nitrate, phosphate diffusions/infiltrating into the groundwater system within the study area is high.

The major problem that has been identified is; anthropogenic influences mainly from agricultural inputs such as fertilizers, pesticides, and manure in the entire catchment.

In literature, the major works done in the study area are sustainable irrigation development (Ofosu, 2011), and climate change impact on smallholder farmers (Amikuzuno, 2013). Therefore, hydrogeochemical and isotopic studies of groundwater in the study area will serve as baseline information for groundwater resource management.

1.3 RESEARCH OBJECTIVES

1.3.1 Main Objective

The main aim of this work is to use geochemical and isotopic techniques to assess the chemical quality of groundwater in the Lower Anayari catchment, focusing on the dominant geochemical processes and anthropogenic activities that influence groundwater chemistry.

1.3.1.1 Specific Objectives

The specific objectives of this study are;

a) to determine the hydrochemical facies of groundwater within the catchment area.

b) to assess the quality of the groundwater in the Lower Anayari catchment area.

c) to investigate the probability of surface-groundwater interactions in the catchment area using environmental isotope techniques [$\delta^{18}O$ and $\delta^{2}H$].

1.4 RELEVANCE AND JUSTIFICATIONS

The chemical nature of groundwater determines it's suitability for consumption. Contamination of groundwater has become an important issue; the sources of contamination can be diffuse or localized. To sustain and maximize the benefit of the groundwater resource, knowledge about the natural hydro-geological, hydro-chemical and geochemical processes, as well as anthropogenic activities on the groundwater resource necessitate a comprehensive and complete scientific understanding of the vulnerability of the aquifers to contamination. Data generated will be useful for decision and policy makers to adopt suitable and practical remedial measures to protect the groundwater sources.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 GEOCHEMICAL STUDIES

Geochemical studies profoundly provide knowledge on the distribution and migration of elements in and between different environmental compartments, and happens to be crucial in understanding pollution that originates from natural and anthropogenic sources (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).

Furthermore, geochemical and hydrochemical studies play a vital role in understanding the controls of groundwater quality. The quality of groundwater is mainly influenced by factors, such as rock chemistry in recharge area, 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).

Factors that controls of groundwater quality are evaporation and evapotranspiration, selective uptake of ions by vegetation, decay of organic matter, weathering and dissolution of minerals, precipitate of minerals, ion exchange reactions, mixing of different water qualities, and anthropogenic activities (Appelo and Postma, 1996b).

Various studies on ground water chemistry have revealed that either some or all of the mentioned factors influence the chemistry of groundwater.

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

Bennetts et al., (2006) also report that dryland salinization in discharge areas in the Willaura catchment in south-eastern Australia, which is affected by both primary (natural) and secondary (human-induced) salinity is as result of; (i) evapotranspiration; (ii) mineral-water interactions within the aquifers which cause a slight overall reduction in salinity; conversion of kaolinite to smectite and illite, and cation exchange of Na^+ for Ca^{2+} on smectites; and, (iii) progressive addition of this saline soil-water to fresher groundwaters recharged on the catchment margins, which has occurred throughout the Holocene.

In four village districts in north-central and northwestern Sri Lanka, Young et al., (2011) reports that high Fluoride concentrations (> 1.5 mg/L), in the study area was influenced greatly by pH and the concentrations of Na, Ca, and HCO_3^-. In addition, their studies highlighted that occurrence of high fluoride concentrations in shallow groundwater although was attributed to longer residence time groundwater in basement rocks aquifers (hornblende biotite gneiss, biotite gneiss, and granitic gneiss), was however related to intensive agricultural activities due to successive irrigation.

Reported work by Zhu et al., (2008) shows that groundwater quality in the Heihe River Basin, China is strongly influence by dissolution of halite, Glauber's salt, gypsum, dolomite and calcite as well as processes such as evaporation, HCO_3 exchange and deposition.

Jiang et al., (2009) used 42 groundwater sampling sites to study groundwater chemistry in the Nandong Underground River System (NURS) in the southeast Yunnan Province, China. The report suggest that, groundwater chemistry evolved from Ca–HCO_3 or Ca (Mg)–HCO_3 type to the Ca–Cl (+NO_3) or Ca (Mg)–Cl (+NO_3), and Ca–Cl (+NO_3+SO_4) or Ca (Mg)–Cl (+NO_3+SO_4) type, indicating increases in NO_3^-, Cl^- and SO_4^{2-} concentrations. The cause of the variations were associated to; (a) contamination from human activities such as sewage effluents and agricultural fertilizers; (b) water–rock interaction in limestone-dominated system; and (c) water–rock interaction in dolomite-dominated system.

Similar, extensive groundwater quality studies using factor analysis and kriging with information entropy theory in Taiwan by Shyu et al., (2011) shows that groundwater quality was strongly influenced by progressing seawater intrusion, industrial wastewater, and to a less extent domestic wastewater.

Similarly, the major cause of groundwater salinization and arsenic pollution in the coastal area of Yun-Lin, Taiwan, was studied by Liu et al., (2003). Report from the study suggested over-extraction of groundwater to be a major cause. The reason was that over-pumping of the local groundwater causes land subsidence and gradual salinization by seawater, and introduction of excess dissolved oxygen that oxidizes the immobile minerals, and releases arsenic by reductive dissolution of arsenic-rich iron oxyhydroxides.

Reported work in India, on the major geochemical processes that regulate groundwater chemistry in Chithar River basin (Subramani et al., 2010). Suggest that, the predominant factors affecting the groundwater chemistry were weathering of carbonate and silicate minerals, ion exchange reactions and the impact of agricultural activities such as irrigation return flow and fertiliser application.

Similar studies by Krishnaraj et al., (2012) in Thirumanimuttar basin, India also suggest that the geochemical evolution of groundwater from Ca-HCO_3 to Na-Cl water types, is largely by ion exchange process, silicate and carbonate weathering along with anthropogenic activities.

The primarily controls of groundwater chemistry in Chhatarpur area, India (Avtar et al., 2013) are reported to be carbonate and silicate mineral weathering followed by ground water–surface water interactions, ion exchange and anthropogenic activities.

In Al Batinah coastal aquifer, Oman, (Askri, 2015) reveals that the principal factors controlling the groundwater chemistry are halite dissolution, reverse ion exchange with clay material and anthropogenic pollutants.

However, Murad and Krishnamurthy, (2004) used chlorine-36 along with oxygen and hydrogen stable isotopes and selected major ions to investigate the factors controlling groundwater quality in the eastern part of the United Arab Emirates. Report from their study suggest that seawater intrusion was not a major control of groundwater quality but rather agricultural practices and weathering of host rocks. Although previous studies in the study area suggest that groundwater quality was influenced by seawater intrusion and evaporation.

Hydrogeological and hydrochemical study conducted on a shallow alluvial aquifer located in the Taif region of western Saudi Arabia by Al-Shaibani, (2008) suggest that groundwater quality is strongly influenced by stream runoff and sewage water. This was evident in their study by significant improvement of groundwater quality after the installation of a concrete runoff tunnel and a wastewater treatment plant.

In Africa, Abid et al., (2011) studied hydrologic and geologic factors controlling groundwater geochemistry in the Turonian aquifer, southern Tunisia. His studies revealed that factors controlling groundwater chemistry in the area were calcite precipitation, gypsum and halite dissolution, ion exchange and mixing of different waters which was revealed using stable isotopes.

Reported work in Plio-quaternary eastern coastal aquifer, Tunisia by Hamouda et al., (2011) reveals the causes of groundwater qualitative degradation were overexploitation of groundwater resulting in sea water intrusion, and irrigation that induces soil leaching and transfer of fertilizers into groundwater system.

Similarly, hydrogeochemical survey on the Mio–Plio–Quaternary aquifer system, Tunisia by Yangui et al., (2011) suggest that the groundwater chemistry patterns and main mineralization processes occurring in the system, are controlled by dissolution of evaporate minerals and evaporation.

Similar work in Chott's region, Tunisia, by Kamel et al., (2008) shows groundwater quality is influenced by dissolution of evaporites and carbonates and to a lesser extent carbonate precipitation, and also interaction with the basinal sediments due the flow pattern and time of residence.

However, reported work in Ethiopia by Demlie et al., (2007), suggest that factors governing the groundwater chemistry following the regional flow direction in Akaki volcanic aquifer system, are dissolution of silicate minerals coupled with precipitation of kaolinite, chalcedony, and rare calcite.

Similar work, in the Senegal River delta aquifer by Diaw et al., (2012) suggest three main hydrochemical facies of groundwater namely Ca–HCO_3, Ca/Na–HCO_3, Na–Cl and Ca/Na–Cl water type, and this consequence from saline intrusion and secondary brines, halite, gypsum and calcite dissolution, and processes such as evaporation, salt deposition, ion exchange and reverse ion exchange reactions.

Detailed hydrogeochemical and isotopic studies of groundwaters from the Hammamet-Nabeul unconfined aquifer, north-eastern Tunisia (Moussa et al., 2011), reveal that control of groundwater of Na-Cl and Ca-SO_4-Cl water facies mineralization were mainly by dissolution of evaporates, dedolomitization, cation-exchange process and anthropogenic process in relation with return flow of irrigation waters.

2.2 PREVIOUS STUDIES IN GHANA AND THE STUDY AREA

In Ghana there have been several works that have employed hydrogeochemistry and environmental isotopes to evaluate recharge processes, understand groundwater flow systems, origin of salinity, and 'age' determination of groundwater. Examples of major works in groundwater geochemistry in Ghana are in (Acheampong and Hess, 1999; Adomako et al., 2010; Akiti, 1980; Anku et al., 2008).

Anku et al., (2008) studied groundwater quality in northern Ghana using 95 groundwater samples, and report that groundwater quality was mainly controlled by the weathering of silicate minerals since they are stable in montmorillonite field. High nitrate (50 to 194 mg/L) was reported to be evident in the western portions of the study area. High fluoride (>1.5 mg/L) concentrations were also recorded at Bongo in the upper east region of Ghana.

Adomako et al., (2010) investigate the geochemistry, the genesis of groundwater flow and its characteristics recharge processes and estimation in the Densu River Basin. Findings from their studies suggest that groundwater flow from recharge to discharge areas, chemically evolves from Ca-HCO_3, Ca/Mg- HCO_3 to Ca/Na-Cl, Ca-Na-HCO_3, and Na-Cl. The evolution is reported to be governed by processes such as weathering of silicate minerals, carbonate dissolution, ion exchange and slight evaporation which seem to be more pronounced down gradient of the flow system.

In the northern part of the Densu River basin, Gibrilla et al., (2010b) used 26 water samples (boreholes, hand-dug well and surface water) to assess the hydrogeochemical processes influencing groundwater quality. The study reports that, groundwater quality parameters were within the WHO recommended values, with the exception of nitrate (NO_3-N). Also, the groundwater chemistry was reported to be Na-Cl or Na-HCO_3-Cl, Na-Mg-Ca-HCO_3 and Na-HCO_3 and Ca-Mg-HCO_3 water types, and this was influenced by factors such as ion-exchange reactions, weathering, oxidation, dissolution of minerals, and some extent extensive agriculture and rapid urbanization in the middle portion of the basin.

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

Ackah et al., (2011) used 16 sampling point to assess the quality of groundwater in Teimen-Oyarifa, Ga west district and reports that it is suitable for irrigation and it chemical constituents are within guidelines for drinking water quality set by both national and international bodies.

In Gushegu district, Northern Region, Salifu et al., (2015) used 19 groundwater sampling points and 7 rock samples to evaluate water quality, water types, and sources of various ions as well as origin of the groundwater. Report show that the groundwater chemistry from the area is of $Na–HCO_3$ and $Na–Ca–Mg–HCO_3$ water type, and was generally influence by rock weathering and precipitation. Also, the study report 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 mg/L).

Hydrogeochemistry of groundwater and surface water in Ellembelle district, western region was studied by Edjah et al., (2015). Thirty eight samples was used to reveal four hydrochemical facies namely, Na-HCO_3 and Ca-Cl-HCO_3 for surface water, Na-Cl, Na-HCO_3, Ca-HCO_3 water type for groundwater. Geochemical processes influencing the chemistry of groundwater and surface water were dissolution of calcite and dolomite precipitations, silicate and carbonate weathering, base-exchange reactions, and evaporation-crystallization which influences the rivers.

Bakobie and Awal, (2015) used 10 hand-dug wells to investigate 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 suggest that although chemical parameters where below WHO recommended guideline for drinking water, coliform bacteria were above WHO limits, hence it's unsuitable for direct human consumption.

The groundwater chemistry in SW Ashanti a mining region in Ashanti region was studied by Bempah et al., (2016). Geochemical process that influence the variation of Ca-Mg-HCO_3 to Na-K-HCO_3 water type were determined to be alumina-silicate weathering, dissolution of carbonate minerals, and ion exchange reaction. Furthermore, dissolution of arsenic-containing minerals were suggested to account for high As and Fe concentrations in the study area.

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; 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.

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

Pelig-Ba, (1998) analysed about 20 trace elements in water samples from 60 boreholes located in the Upper East and West Regions of Ghana. His findings indicated that most trace element concentrations were higher as compared to their concentrations found in natural water systems. The occurrence of these trace elements in the analysed water samples was associated to the local bedrock as the dominant source of the trace elements. Furthermore, Al, Fe, Mn, Zn, Sr, and Ba concentrations from his finding were excessively high, in comparison with WHO guidelines.

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

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

In Atankwidi sub-basin, a neighbouring sub-basin to Lower Anayari sub-basin Barnie et al., (2014) assessed the quality of shallow groundwater for irrigation using the relationship between sodium absorption ratio (SAR) and salinity (EC) hazard (USSL salinity diagram), magnesium hazard and alkalinity. In their study, 40 wells was used, and two main water types (Ca-Mg-HCO_3 and Na-Mg-Ca-HCO_3) were identified. The relative abundance of cations and anions in groundwater were reported to be in the decreasing order of $Na^+ > Ca^{2+} > K^+ > Mg^{2+} > Fe^{2+}$ and $HCO_3^- > SO_4^{2-} > Cl^- > PO_4^{2-} > NO_3^- > F^-$ respectively. Conclusion from their study were that the suitability of groundwater for irrigation, evaluated based on sodium (SAR), salinity and magnesium hazards, pH and alkalinity, are good for irrigation but with some potential magnesium hazard and alkalinity problems which can partially limits its use for irrigation since the likelihood of developing sodic soil conditions with continuous use are high.

2.3 GROUNDWATER QUALITY

Groundwater is commonly considered safe for consumption, for pathogenic organisms cannot survive at very great depths below the earth (Pelig-Ba, 1998). However, some dissolved constituents do not depend on depths of groundwater and can pose health problems when it is in high concentration (Pelig-Ba, 1998). The dissolved constituents range from major constituents (> 5 mg/L) to trace elements (< 0.1 mg/L) (Freeze and Cherry, 1979b).

2.3.1 Parameters

2.3.1.1 Electrical Conductivity

This measures 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, multiplication factor close to 0.67 are usually for waters in which Na and Cl ions dominate, and for higher for waters containing high concentration of SO_4. The conductivity of most fresh water ranges from 10 to 1000 µS/cm. Electrical conductivity have used in some studies to establish a pollution zone (Chapman and Kimstash, 1996).

2.3.1.2 pH

The pH is a measure of the acid balance of a solution at a given temperature (Hill, 2000). 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 humic and fulvic acids (Chapman and Kimstash, 1996). pH of most natural waters ranged between 6.0 and 8.5, lower values can occur in dilute waters high in organic content.

2.3.1.3 Sodium

It 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 atmosphere, feldspar, rock-salt (halite), zeolite, and mirabillite (Appelo and Postma, 1996b). Elevated sodium in groundwater used for irrigation in certain soil types can degrade soil structure thereby restricting waste movement and affecting plant growth. The sodium adsorption ratio (SAR) is used to evaluate the suitability of water for irrigation and this estimates the degree to which sodium is adsorbed by the soil. High values of SAR imply that the sodium in the irrigation water may replace the calcium and magnesium ions in the soil, potentially causing damage to the soil structure. Examples of works in which sodium adsorption ratio (SAR) have been used in evaluation the suitability of water for irrigation purposes are in (Gibrilla et al., 2011; Nagaraju et al., 2016; Peiyue et al., 2011; Singh et al., 2015; Tiwari and Singh, 2014).

2.3.1.4 Potassium

It is found in low concentration in natural waters since rocks which contain potassium are relatively resistant to weathering (Chapman and Kimstash, 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 Kimstash, 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).

2.3.1.5 Calcium

Is present in all waters for it readily dissolves from rocks rick in calcium minerals (Ca-feldspar, pyroxene, amphibole) (Appelo and Postma, 1996b; Chapman and Kimstash, 1996). Calcium concentration in natural waters are generally < 15 mg/L, however, may reach concentrations 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 Ca and contribute about 80% or more on a global scale (Garrels, 1975). Only about 10% 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 $Ca(NO_3)_2$ fertilizers (Stigter et al., 2006).

2.3.1.6 Magnesium

Magnesium is common in natural waters as Mg^{2+}, and along with calcium. It principally arise 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 pryrite 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).

2.3.1.7 Carbonates and Bicarbonates

Carbonates and bicarbonate content in natural water arise from soil CO_2- pressure (atmosphere and biological respiration) and weathering (Appelo and Postma, 1996b; Chapman and Kimstash, 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, like dissolution of calcite and dolomite are the primary source of carbonate and bicarbonate ions in groundwater (Chapman and Kimstash, 1996; Mazor, 1975).

2.3.1.8 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, sylivte) 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 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).

2.3.1.9 Nitrate

The nitrate ion (NO_3) is the common form of combined nitrogen found in natural waters. Natural sources of nitrate to surface waters include igneous rocks, land drainage, plants and animals debris (Chapman and Kimstash, 1996; Younie et al., 1996). Nitrate in groundwater results from soil leaching and also leaching in areas of high nitrogen fertilizer. Generally, nitrate concentration in groundwater are low, however, concentrations in excess of 5 mg/L are associated to pollution by human and animal waste, or fertiliser run-off (Chapman and Kimstash, 1996; Younie et al., 1996). High concentration (200 mg/L) of nitrate in groundwater have been related to increased fertilizer applications (Akiti, 1982; Chapman and Kimstash, 1996; Fianko et al., 2008; Jeyaruba and Thushyanthy, 2009; Munster, 2008; Younie et al., 1996).

Nitrates levels in drinking water above legal limits could result in detrimental effects such as cancer, methemoglobinemia, birth defects and disruption of thyroid functions (Kubreziga, 2012).

2.3.1.10 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 ($CuFeS_2$), pentlandite [$(NiFe)_9S_8$], and pyrite, epsomite, mirabillite, 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).

2.3.1.11 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).

2.3.1.12 Phosphorus Compounds

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- P, and arise in natural water mainly from the weathering of phosphorus-bearing rocks and decomposition of organic matter. However, domestic waste-water (particularly those containing detergents), industrial effluents and fertiliser run-off contribute to elevated levels in surface waters (Chapman and Kimstash, 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-P in some pristine waters and as high as 200 mg/L PO_4-P in some enclosed saline waters (Chapman and Kimstash, 1996).

2.3.2 Water Quality Studies

The intricate process of assessing water quality have 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, most researcher 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 shows that groundwater quality varied as "excellent" and "good" water quality using WQI. 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 Vea Dam suitability 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 assessment. The weighted arithmetic index method calculation of the WQI used was found to be 54.21 indicating poor quality.

2.4 ENVIRONMENTAL ISOTOPES STUDIES IN GHANA

Groundwater studies using environmental isotopes in Ghana was pioneered in 1980s (Akiti, 1980). Later studies on isotopes focused on origin of groundwater (Acheampong and Hess, 2000; Pelig-Ba, 2009), identification of sources of dissolved ions (geogenic and anthropogenic) in groundwater (Gibrilla et al., 2010a; Zakaria et al., 2012), groundwater recharge (Adomako et al., 2010; Fynn et al., 2016), Volta lake and groundwater interaction (Kaka et al., 2011), role of meteoric recharge in the Voltain basin (Yidana, 2013), tracing stable isotopes (δ^2H and $\delta^{18}O$) 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 (δ^2H) and oxygen ($\delta^{18}O$) 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 $\delta^{18}O$ in most of the groundwater (-3.61 to -2.17 ‰ vs VSMOW), depleted in heavy-isotope were located 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%, 28%, 25%, 18%, 16% and 12% respectively.

CHAPTER THREE

3.0 MATERIALS AND METHODS

This Section is divided into six (6) parts (Section 3.1 to Section 3.6). Section 3.1 is a description of the study area. Data collection and Field work are presented in Sections 3.2 and 3.3 respectively. Section 3.4 is a description of Laboratory measurements. Methods used in geochemical data analysis are presented in Section 3.5. Quality assurance and Quality control measures employed in the study are presented in Section 3.6.

3.1 STUDY AREA

3.1.1 Geographical Location of Lower Anayari Catchment

The study area is the Lower Anayari catchment located in the Upper East Region of Ghana. It is a sub-basin of the White Volta basin and covers an area of about 178.4 km^2 (Ofosu, 2011). The Lower Anayari catchment constitutes about forty per cent (40%) of the Anayari catchment. The other portion (60%) of the catchment is located in Burkina Faso.

The Lower Anayari catchment is located partly in the Kassena-Nankana East Municipal and Kassena-Nankana West District. The catchment is between Navrongo (the capital town of Kassena-Nankana Municipal) and Sumbrugu [11 km away from Bolgatanga (the Upper East regional capital town)]. The catchment lies between latitude 10^{o}50’0” N to 11^{o}0’0” N and, longitude 1^{o}7‘30” W to 0^{o}57’30” W. The Lower Anayari catchment is made up six (6) principal communities (Fig 3.1). Each principal community is made up of a host of smaller communities.

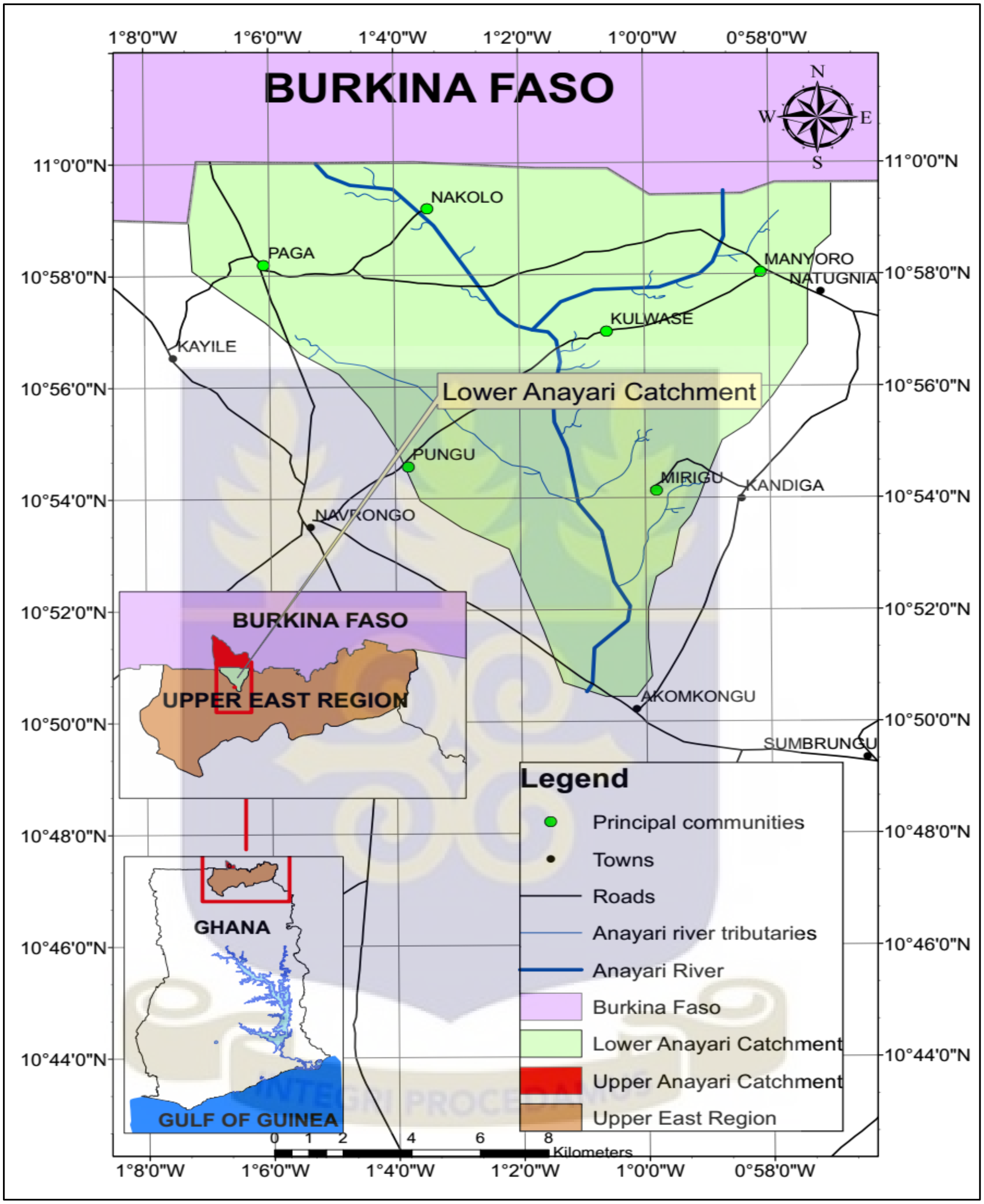

Fig 3.1: Map of the Lower Anayari Catchment (Inset: Map of Ghana showing Upper East Region)

3.1.2 Climate, Drainage and Vegetation

The climatic condition of Lower Anayari catchment is mainly semi- arid. It has a mono-modal rainfall distribution which approximately begins in early May and ends in late October. The mean annual rainfall of Navrongo which is closest town to the catchment is about 993 mm (calculated from average monthly rainfall data from 1980 to 2008 obtained from Navrongo Meteorological Service Department). The highest temperatures are usually observed from early March, while the lowest temperatures occur in December and January. The low temperature is caused by the harmattan winds. High relative humidity is observed during the rainy season around 65% and decreases rapidly to less than 10% after the end of the rainy season in October (Martin, 2006).

The Anayari River takes it sources from Burkina Faso, and flows through the Nakolo community to the Doba community and finally joins with the Atankwidi river southwards. The tributaries of the Anayari River stretch in communities around Pungu and Mirigu community (Fig 3.1).

The vegetation of the study area is characterized mostly by moderately dense herb and bush with scattered trees (Sudan savannah) and less grassland with or without scattered trees and shrubs (SNC-Lavalin, 2011; S.R.I., 1964b). Drought-resistant trees such as acacias, mango trees, sheanut trees, neems and baobabs are usually found in the study area. Land is usually used for small-scale rain-fed agriculture in the form of bush or compound farming. Bush farms are generally located approximately within 10 km of the community, a mixture of cereals/vegetables crops particularly maize, sorghum, millet, and rice; yam, cassava and groundnuts are generally cultivated. Compound farms are mostly located near the homes of the farmer. Crops grown generally include maize and vegetables. After harvesting, agriculturally used lands are left bare until the next rainy season. Land not used for agriculture is either sparse vegetation on shallow soils in stony areas or land used for the grazing of livestock's (Martin, 2006).

3.1.3 Soil

According to Soil Research Institute (SRI), (1964) of the Council for Scientific and Industrial Research (CSIR) of Ghana the soil types found in the study area are; Bianya association, Kolingu association, Nangodi association, Siare-Dagare Complex, and Tanchera association (SRI, 1964) [Fig 3.2]. The Bianya association are light grey fine sandy clay soils derived from grey-wackes and quartz-sericite schists; in valley bottoms they are very dark grey clays. The Kolingu association are moderately eroded, brown or pale brown coarse sandy loams associated with hornblende or biotite granites; frequent stones occur on ground surface; in valley bottoms they are grey sandy loams and clays. Nangodi association are very brashy soils derived from greenstones, andesites, schists and amphibolites occurring on lower to middle slopes of hills; on valley slopes and bottoms they are olive grey or very dark grey clays. Siare-Dagare Complex are distributed along the Anayari River and its tributaries, and consist of a mixture of loose coarse sand and silty loams, and plain alluvium consisting of yellowish grey and dark grey calcareous clays. The Tanchera association are largely distributed within the study area and are moderately deep, pale brown coarse sandy loams associated with biotite granites; in valleys they are grey sandy loams and clays.

Generally, the organic matter content of the soils in the study area are usually low as a consequence of high temperatures and annual burning of vegetation (SNC-Lavalin, 2011).

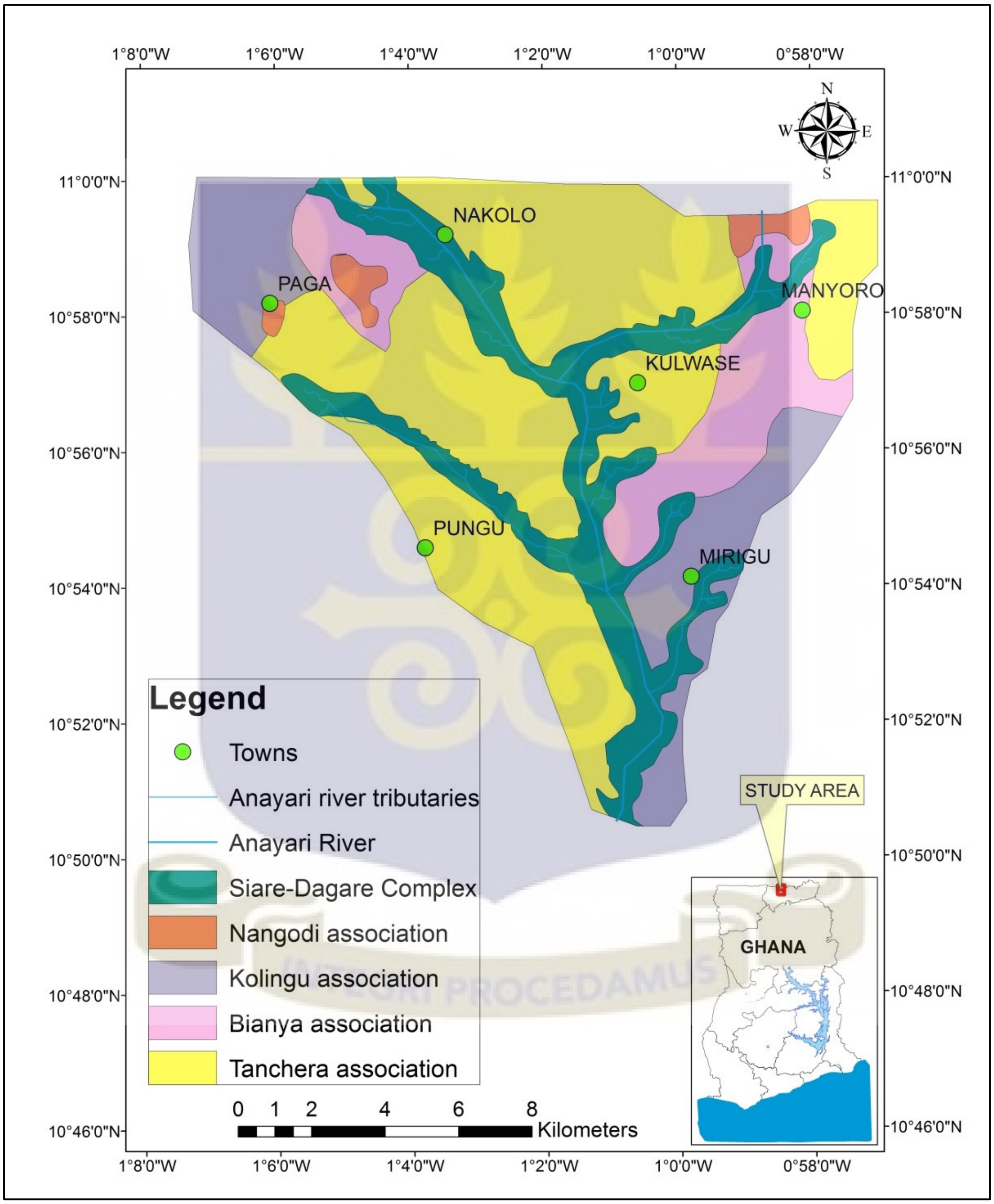

Fig 3.2: Soil Map of Lower Anayari Catchment (Inset: Map of Ghana showing study area). [Source: SRI, (1964)]

3.1.4 Geology

The Lower Anayari catchment is underlain mainly by the Birimian Supergroup strata of volcanic rocks and synvolcanic intrusive rocks. In general, rocks of the Birimian Supergroup consist mainly of volcanic and metavolcanic material. These rocks are strongly foliated and are intruded by large granitoid masses during the Palaeoproterozoic (SNC-Lavalin, 2011). The main rocks in the study area are biotite granitoid and volcanic flow/subvolcanic rock and minor interbedded volcaniclastics (GGS, 2009). The biotite granitoid rocks cover a larger portion of the catchment (about 90%) and are undifferentiated and mostly granodiontic. Subvolcanic rock covers a small area at the North West, and across the South west to north east portion of the catchment (Fig 3.3). These rocks are minor interbedded volcaniclastic and are undifferentiated.

Rocks in the study area are overlain by a regolith comprising in situ chemically weathered material and, to a lesser extent, transported surface material. The thickness of the regolith generally ranged between less than 30 m to 60 m (SNC-Lavalin, 2011). Weathering processes as a result of chemical weathering of bedrock usually exhibits a progressive degradation from fresh bedrock to residual soil. The typical zones forming the weathered profile are: (i) residual soil (usually sandy-clayey material); (ii) saprolite (completely to slightly decomposed rock with decreasing clay content with depth); (iii) saprock (fragments of unweathered bedrock in an altered matrix); and, (iv) fresh (inconsistently fractured) bedrock (Chilton and Foster, 1995).

The first two zones namely, residual soil and saprolite form the regolith while the saprock is usually considered as a part of bedrock.

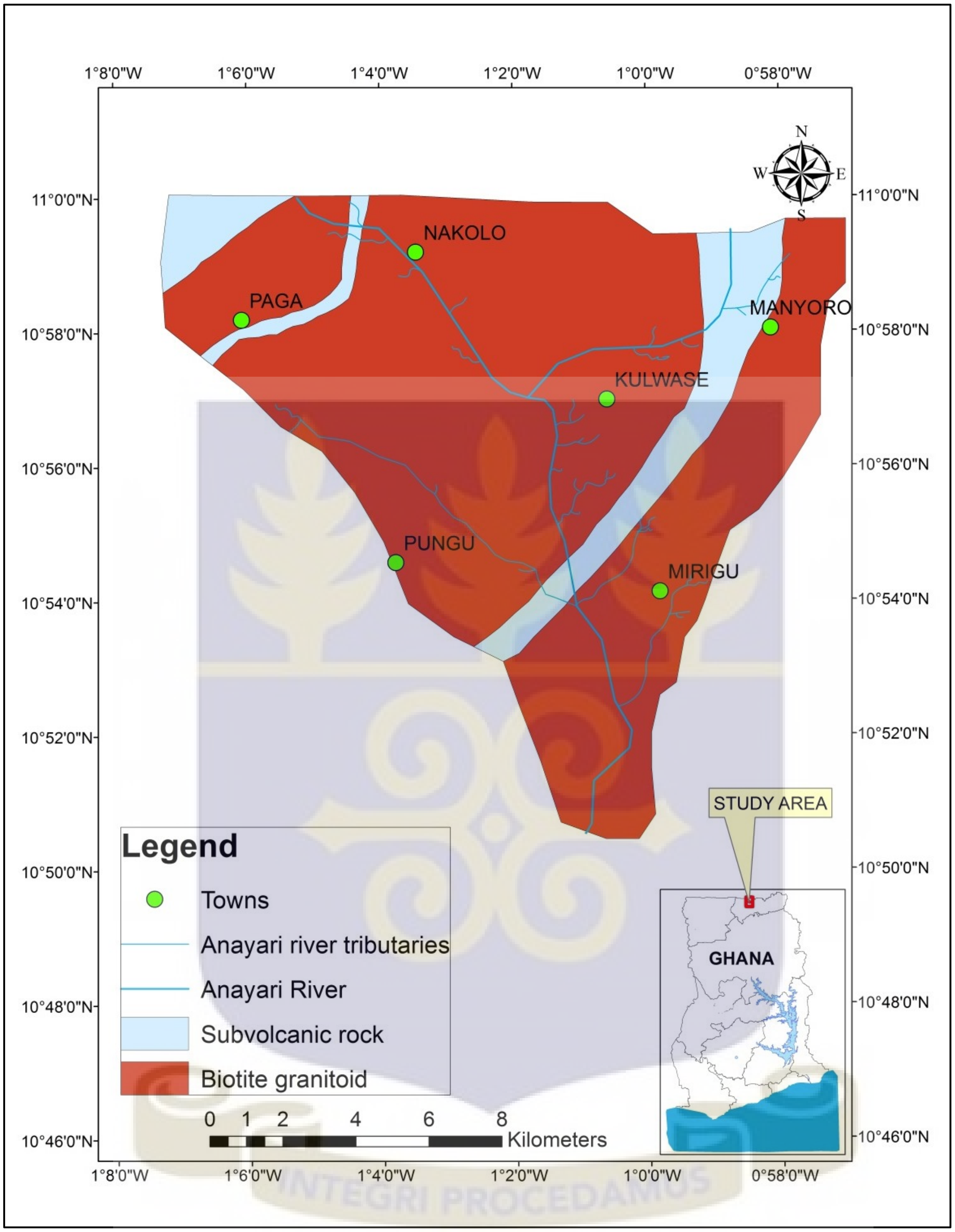

Fig 3.3: Simplified Geological Map of Lower Anayari Catchment (Inset: Map of Ghana showing study area) [Source: Ghana Geological Survey (GGS), 2009]

3.1.5 Hydrogeology and Groundwater Occurrences

In the Lower Anayari catchment, the dominant hydrogeology is the Precambrian basement (PCB) rocks. The rocks of the Precambrian basement (PCB) usually have low primary porosities and permeabilities. However, groundwater occurrence and flow in such basement rocks are mainly controlled by secondary porosity as a result of chemical weathering, faulting and fracturing (from tectonic activity and isostatic uplift) (SNC-Lavalin, 2011). Available literature suggest that on average, areas underlain by rocks of the Birimian Supergroup [Precambrian basement (PCB) rocks] exhibit deeper weathering [about 23 m] (Nathan and Harris, 1970), and weathering is known to have a significant impact on water storage capacity of crystalline rocks (Larsson, 1984). Also, available data suggest that vital sub-vertical fracture or fault zones originating from tectonic activity may occur at great depths (> 150 m) in these rocks which help provide significant amounts of groundwater. Averagely, borehole depth is reported to be less than 80 m in Precambrian basement of which the study are falls within (Agyekum, 2004).

The main aquifer is suggested to be comprised of regolith aquifer, and deep fractures rock aquifer (Martin, 2006). Other researchers describe three basement aquifers systems for similar aquifer type: (i) a shallow, perched aquifer (sandy layer covering the less permeable clay material); (ii) the principal regolith; and, (iii) fractured aquifer (Wilkes et al., 2004).

The shallow aquifer is discontinuous with an average thickness of about one meter. It dries up during the dry season and is only targeted for water supply by traditional hand dug wells. While the regolith and the fractured bedrock aquifers form an integrated aquifer system. The regolith aquifer can exhibit a higher transmissivity than the fractured rock aquifer because of its greater saturated thickness generally (SNC-Lavalin, 2011). In Precambrian basement rocks, transmissivity ranges from 0.1 to 143.3 m^2/d with an average of 16.6 m^2/d, and average specific capacity of 9.4 L/min·m.

3.1.6 Socio-Economic Activities

The study area has an estimated population of about 19,445 according the 2010 Population and Housing Census [Ghana Statistical Service (GSS), 2013]. The occupation of majority of the people is rain-fed farming, alongside small scale animal rearing, petty trading and, traditional cloth weaving. The main types of crops cultivated include millet, groundnut, rice, sorghum, cowpea, vegetables (tomatoes, pepper) and maize. Some farmers practice traditional irrigation farming along river banks on during the dry season. The main irrigated crops are tomatoes and pepper. From field survey, most farmers apply manure on their farms while some vegetables and rice farmers apply inorganic fertilizers. Others also apply mixture of organic manure and inorganic fertilizer. The manure type applied mainly include the cow and donkey dung, sheep and goat droppings and their mixtures and on some occasions fowl droppings. The main inorganic fertilizers applied are the NPK 15:15:15 and Ammonia (NH_3). Attempts made to estimate the quantity of manure or fertilizer applied per farm size per year proved difficult as most of the farmers could not provide the estimated amounts they use yearly per the size of their farms.

The major use of groundwater in Lower Anayari catchment is largely for domestic purposes. The use of groundwater for irrigation purposes is minimal. Other uses of water in the catchment area are for feeding farm animals, building and repairing of mud houses.

3.2 DATA COLLECTION

Prior to sample collection, data related to the study to be undertaking at 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.

3.2.1 Desk Study

A desk-study was carried out to assess the general hydrological and hydrochemical facies prevailing in the surface and groundwater around Lower Anayari Catchment.

This task involved literature review, collection of topographical maps, collection of data from Ghana Meteorological Agency, Navrongo and the Geological Survey Department (GSD). The study also involved the assessment of equipment required for measurement of key physico-chemical parameters on the field.

3.2.2 Reconnaissance Field Work

A Two-week reconnaissance field survey was carried out prior to actual sampling, to identify the sampling points, the type of kits that were required for the sampling task, to identify the types of surface water (rivers, and irrigation dams) and, groundwater (hand-dug wells and boreholes) to be collected.

3.3 FIELD WORK

3.3.1 Sampling

3.3.1.1 Sampling containers

Three hundred millilitre (300 mL) polyethylene containers (bottles) used for collection of waters samples for assessment of hydrochemical parameters were prepared for sampling by immersion in 10% (v/v) HNO_3 solution for 48 hours, and thoroughly rinsed with double-distilled water before use (Sundaram et al., 2009). One hundred millilitre (100 mL) polyethylene containers (bottles) were used to collect sample water for stable isotope studies. In addition, a secondary polyethylene container was used to aid sampling of surface water and also sampling for stable isotopes studies.

3.3.1.2 Boreholes, Hand-dug wells, River and Dams sampling

A total of sixty-six (66) water samples were collected from equipped boreholes, hand dug wells, irrigation ponds/dams and river across the catchment between September 2015 and October 2015. The sampling period was in the rainy season. At each sampling point, three (3) replicate water samples were collected for hydrochemical studies, stable isotope studies, and trace metals determination respectively. For quality control (QC) purposes, additional samples (apart from the three replicates) were collected randomly at some sampling points (Table 3.1). This was done to check analytical precision of sampling and analysis. Summary of number of water samples collected and description of sampling site are shown in Table 3.1 and Table 3.2 respectively.

Standard procedures with regard to well purging were followed for the collection of the groundwater samples as outlined in (IAEA, 2010; Sundaram et al., 2009). Samples from the Anayari River and Irrigation Dams in the study area were collected using a polyethylene container. Samples were collected under water, about 10 m away from the banks of the water source (river or irrigation dam).

Samples for hydrochemical studies were filtered through a 0.45 µm membrane filter into acid-washed 300 mL polyethylene bottles, tightly sealed and stored in thermos insulated containers with ice pack.

Samples for heavy metals analyses were filtered through a 0.45 µm membrane filter into 300 mL acid-washed polyethylene bottles and were acidified by adding two drops of 70% (w/v) nitric acid and tightly sealed.

Samples for ^{18}O and ^{2}H analysis were collected by filling the 100 mL bottles from a secondary polyethylene container. It was tightly sealed underwater, wipe dry, retightened and tape capped using an electrical tape in a clockwise direction. This was done carefully to avoid air bubbles. They were then labelled carefully with the relevant information about the sample. The geographical locations of all sampling points were recorded using a hand-held Global Positioning Systems (GPS) [Fig 3.4].

3.3.1.3 Storage and Transportation of Water Samples

Samples for hydrochemical parameters and trace metals determination were stored in thermos-insulated containers with ice packs. Water samples for isotopic studies were kept in separate thermally-insulated container without ice packs. They were then transported over night from Navrongo to the laboratories of the Ghana Atomic Energy Commission, Kwabenya, Accra.

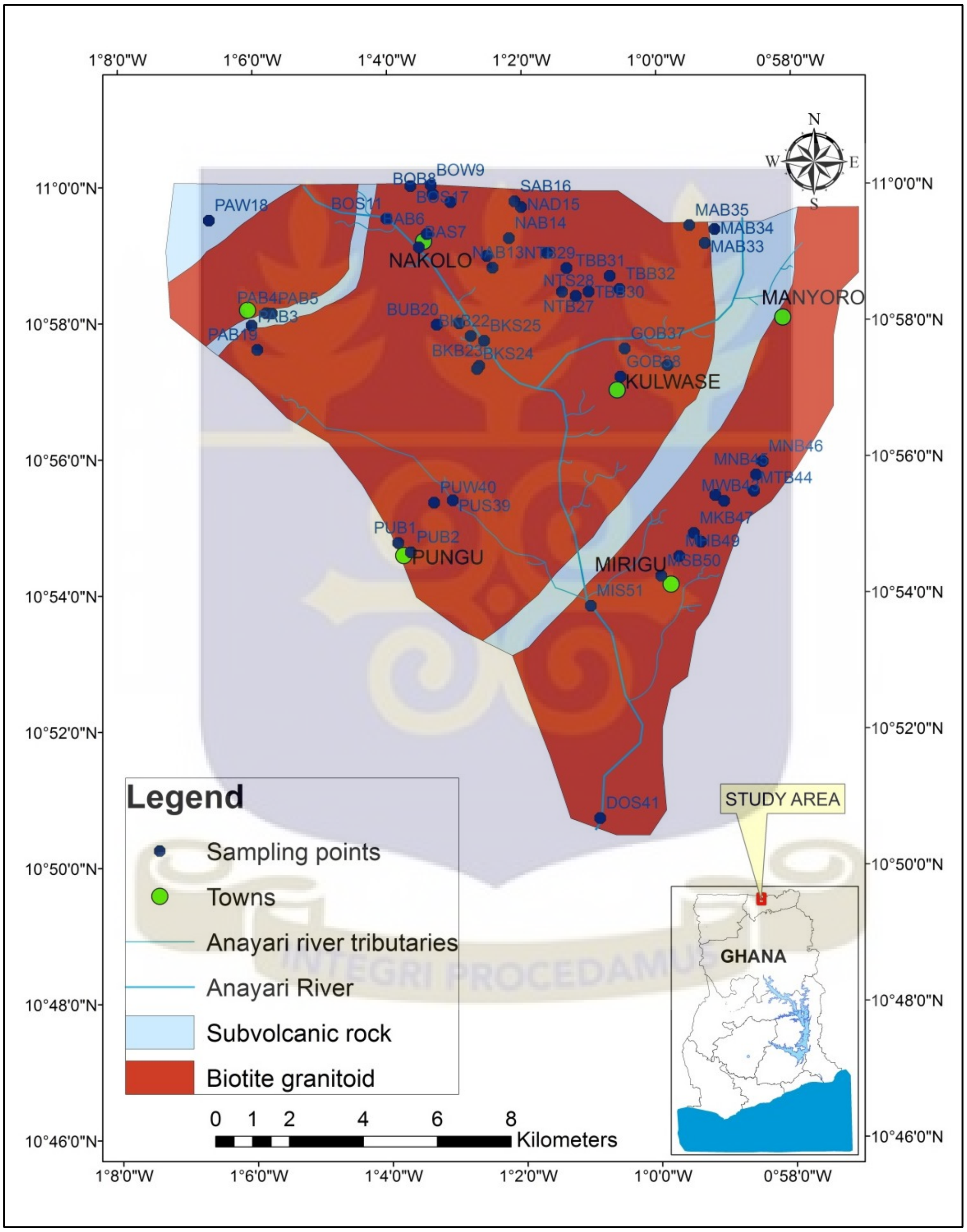

Fig 3.4: Map of Lower Anayari Catchment showing sample collection points (Inset: Map of Ghana showing study area).

Table 3.1: Summary of sample types and number of samples collected

Sample types	Number of samples collected	
	Number of samples (Original)	Additional samples
Groundwater	37	8
Irrigation Dams	4	2
Wells	4	2
Anayari River	6	3

Table 3.2: Description of sampling site

Sampling Town	Water Source	Sampling Site/code	Geology	Information about sampling sites
Banyono	Borehole	BAB6	Biotite Granitoid	Millet farm within the vicinity
	River	BAS7	Biotite Granitoid	No trees by the river bank, maize farm about 100 to 450 m away from the river bank
Boania	Borehole	BOB8	Biotite Granitoid	By the road; close to a house; few trees and millet farm around about 50m
	Borehole	BOB10	Biotite Granitoid	Sited under a tree; houses close by
	Irrigation Dam	BOS17	Biotite Granitoid	Trees around; purposely used as livestock water source and irrigation
	River	BOS11	Biotite Granitoid	The sides are highly eroded; Used purposely for laundry; Kids swimming in the river;
	Hand-dug well	BOW9	Biotite Granitoid	Covered and about 30% exposed, corn and millet farm within the vicinity
Buru	Borehole	BUB20	Biotite Granitoid	Sited close by a chief palace; Millet and maize farm close to the well.
	Borehole	BKB22	Biotite Granitoid	Sited in a school; and few trees close to the borehole
	Borehole	BKB23	Biotite Granitoid	Sited in a school; no trees within the vicinity
	Irrigation Dam	BKS24	Biotite Granitoid	Few trees within the vicinity; Source of water is purposely used for livestock and irrigation; very close to a school where BKB23 is sited
	River	BKS25	Biotite Granitoid	Very open and few farms along the river banks;
	Hand-dug well	BUW21	Biotite Granitoid	Site very close to a house, a pen and maize farm; and not properly covered
Doba	River	DOS41	Biotite Granitoid	No trees by the river bank, only grass along the banks

Table 3.3: Description of sampling site (continuation)

Sampling Town	Water source	Sampling Site/code	Geology	Information on sampling site
Gomowo	Borehole	GOB36	Biotite Granitoid	Sited on a very open area, no trees close to borehole, only few grass
	Borehole	GOB37	Biotite Granitoid	on a clear area; few trees within the vicinity
	Borehole	GOB38	Biotite Granitoid	Millet farm close to borehole
Manyoro	Borehole	MAB33	Biotite Granitoid	Very close to trees
	Borehole	MAB34	Subvolcanic Rock	Borehole is fenced; maize farm close to borehole
	Borehole	MAB35	Biotite Granitoid	On a plain land; millet farm about 100 m away from the borehole.
Mirigu	Borehole	MWB42	Biotite Granitoid	Sited in a school; No trees within the vicinity;
	Borehole	MWB43	Biotite Granitoid	Millet farm close to borehole
	Borehole	MTB44	Biotite Granitoid	Millet and maize farm within the vicinity; organisms found in the water.
	Borehole	MNB45	Biotite Granitoid	In the market; no trees within the vicinity
	Borehole	MNB46	Biotite Granitoid	Borehole sited in a school; No trees close by
	Borehole	MKB47	Biotite Granitoid	Millet farm close to borehole
	Borehole	MKB48	Biotite Granitoid	Millet farm within the vicinity
	Borehole	MHB49	Biotite Granitoid	Sited near Community health post; few millet farm close to borehole.
	Borehole	MSB50	Biotite Granitoid	Sited In a school and by the road side
	River	MIS51	Biotite Granitoid	very open and quite large; no trees sited at the river bank

Table 3.4: Description of sampling site (continuation)

Sampling towns	Water source	Sampling site/code	Geology	Information on sampling site
Nakolo	Borehole	NAB12	Biotite Granitoid	Sited under a tree
	Borehole	NAB13	Biotite Granitoid	Millet and corn farm and a house close to borehole
	Borehole	NAB14	Biotite Granitoid	Sited by the road side; trees within the vicinity
	Borehole	SAB16	Biotite Granitoid	Millet farm close to borehole.
	Irrigation Dam	NAD15	Biotite Granitoid	Millet farm within the vicinity; cattle grazing around, and drink from it.; Very open place; it is used for irrigation purposes
Navior-Tazika	Borehole	NTB26	Biotite Granitoid	Rice and millet farm close to borehole
	Borehole	NTB27	Biotite Granitoid	Groundnut farm within the vicinity
	Borehole	NTB29	Biotite Granitoid	Millet farm close to borehole
	Irrigation Dam	NTS28	Biotite Granitoid	Trees in the dam; purposely livestock water source and irrigation
Paga	Borehole	PAB3	Subvolcanic Rock	Farm (millet and groundnut) within the vicinity
	Borehole	PAB4	Subvolcanic Rock	Sited by the road; houses close to the borehole
	Borehole	PAB5	Subvolcanic Rock	Sited by the road; a millet farm 50 m away from the borehole
	Borehole	PAB19	Biotite Granitoid	Sited by the main road side; corn farm within the vicinity.
	Hand-dug well	PAW18	Subvolcanic Rock	By the road side and washing bay close by
Pungu	Borehole	PUB1	Biotite Granitoid	Sited by the road side and football park within the vicinity
	Borehole	PUB2	Biotite Granitoid	farm (millet and corn) close to borehole
	River	PUS39	Biotite Granitoid	No trees along the river bank; people usually cross by foot, bicycle and motorcycle.
	Hand-dug well	PUW40	Biotite Granitoid	Sited close to the road side, Pungu solar plant and a latrine.
Tazika-Batua	Borehole	TBB30	Biotite Granitoid	Sited under a trees; Near a school.
	Borehole	TBB31	Biotite Granitoid	Groundnut farm within the vicinity
	Borehole	TBB32	Biotite Granitoid	Groundnut farm very close to the borehole

3.3.2 Measurement of Field Parameters

Bicarbonate [HCO_3^-] Alkalinity and physical parameters like Electrical Conductivity (EC), Total Dissolved Solids (TDS), Salinity, Temperature and pH of samples were measured on-site after collection of the water samples using potable conductivity and pH meters. Bicarbonate [HCO_3^-] Alkalinity of water samples were determined by titrimetry.

3.3.2.1 Bicarbonate (HCO_3^-) Alkalinity

Alkalinity and bicarbonate contents of the water samples (surface water and groundwater) were determined by titrimetry using HCl as titrant and methyl orange indicator (Fig 3.5).

The alkalinity of water is attributed to the presence of caustic alkalinity $[HCO_3^-, CO_3^{2-}, B(OH)_4^-, OH^-, H_3SiO_4^-, HS^-, organic\ anions]$ (Drever, 1982a). Alkalinity is therefore a measure of ability of water to neutralize acids. However, in most natural waters, borate, ionised silicic acid, bisulphide, and organic anions are present in very small concentrations compared with dissolved bicarbonate and carbonate ions. Hence the most important definition of sample alkalinity is:

$$\text{Alkalinity} = m_{HCO_3^-} + 2m_{CO_3^{2-}} \tag{3.1}$$

where *m* is molarity (Drever, 1982a; Hill, 2000; Trevor, 1990).

In the determination of total alkalinity, the contents of HCO_3^-, CO_3^{2-} were estimated together by titration against a standard acid (HCl) using methyl orange as indicator. The determination is based on the following reactions as shown in equations;

$$H^{+}_{(aq)} + CO^{2-}_{3\,(aq)} \longrightarrow HCO^{-}_{3(aq)} \qquad (3.2)$$

$$H^{+}_{(aq)} + HCO^{-}_{3\,(aq)} \longrightarrow CO_{2\,(g)} + H_2O_{(l)} \qquad (3.3)$$

About 25 mL aliquot of the water sample was transferred into a 125 mL conical flask. This was followed by the addition of two drops of methyl orange indicator. The contents of the conical flask were swirled to mix thoroughly (a yellow colour was developed). The water sample was then titrated against 0.02 M HCl solution, till the yellow colour changed to orange (signifying the end point of the titration). The volume of titrant (HCl) used was recorded. Two replicate titrations were carried out to obtained consistent titre and were averaged.

The pH of samples for the study area was less than 8 indicating HCO_3^-as the dominant species (Trevor, 1990).

Hence, the concentration of HCO_3^- in mg/L was calculated from the equation below;

$$[HCO_3^-] = \frac{V_{HCl} \times C_{HCl} \times M_{HCO_3^-}}{A} \qquad (3.4)$$

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 $M_{HCO_3^-}$ is molar mass of HCO_3^-

Fig 3.5: On-site Alkalinity determination

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

The Hanna HI 991301 multi-functional conductivity meter was used to determine Electrical conductivity (EC), Total Dissolved Solid, Salinity, and Temperature of water samples. Prior to measurement, the meter was calibrated using three standard KCl solutions of conductivities 84 µS/cm, 1814 µS/cm and 5000 µS/cm. The electrode was rinsed in distilled water followed by sampled water. The electrode was dipped into the sample and was slowly moved circularly for a minute until digital readout was stabilised.

3.3.2.3 pH

The HACH pH meter was used to determine pH measurements of water samples on-site. This was done by dipping the electrode into groundwater sample collected in sample bottle and covered with clear-wrap. This was done to reduce the degree of changes that might occur since once the sample is extracted from the aquifer, physical controls governing the H^+ activities changes and leads to changes in pH (Trevor, 1990). Digital readout was taken when readout was stabilised. Before pH of water samples was determined, the instrument was calibrated using buffer solutions of pH 4.01 and 7.00.

3.4 LABORATORY MEASUREMENTS

3.4.1 Chemical Analysis

3.4.1.1 Major and Minor Anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, and SO_4^{2-})

Levels of anions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}) were determined using Dionex ICS-90 Ion chromatograph (Fig. 3.6) at Inorganic Chemistry Laboratory, GAEC, Kwabenya, Accra. The IC performs isocratic ion analyses using supressed 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 on the basis of 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 on the basis of 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).

Fig. 3.6: Sample injection into ICS-90 using 1mL syringe

3.4.1.2 Major cations hydrochemical parameters

3.4.1.3 Calcium (Ca^{2+})

Determination of Ca^{2+} ions in water samples was done using complexometric titration (EDTA method) at the Inorganic Chemistry Laboratory, GAEC, Kwabenya, Accra.

In complexometric titration, a metal ion reacts with a suitable ligand to form a complex, the equivalence point of the titration is determined by an indicator. The EDTA (ethylenediaminetetraacetic acid or its salts) in water containing calcium are able to form complex, and in the presence Murexide (ammonium purpurate) indicator changes from pink to purple indicating end point of the reaction, when all of the calcium has been complexed by the EDTA at a pH of 12 to 13.

Twenty-five millilitres (25 mL) of water sample was pipetted into a conical flask and 2.0 mL NaOH solution was added, followed by stirring for basic conditions (pH 12 to 13) to be attained. This was followed by adding about 0.1 g of murexide indicator to the mixture. The EDTA titrant was then titrated against the water samples, with continuous swirling to obtain proper end point. The volume of EDTA used to reach end point was read as titre. The procedure was repeated for three times to obtain consistent titre and averaged.

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

$$Ca^{2+}_{(aq)} + Y^{4-}_{(aq)} \longrightarrow CaY^{2-}_{(aq)} \tag{3.5}$$

where,

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

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

$$[\mathrm{Ca}^{2+}] = \frac{V_{\mathrm{EDTA}} \times C_{\mathrm{EDTA}} \times M_{\mathrm{Ca}^{2+}}}{V_{\mathrm{sample}}} \qquad (3.6)$$

where,

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

3.4.1.4 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. The instrument, consist of a light source (hollow-cathode lamp), a flame atomizer system (Air- Acetelyene), monochromator or filter and adjustable slit (a means of isolating an absorption line) and a photoelectric detector with its associated electronic amplifying and measuring equipment.

Sub-stock solution (10 mg/L) was prepared by diluting 1 mL of stock solution (1000 mg/L Mg) with distilled water into 100 mL solution. Three working standard (0.1, 0.2 and 0.5 mg/L) were prepared by diluting 1, 2, and 5 mL each of the sub-stock solution with distilled water into 100 mL solution and they were used to calibrate the instrument. After calibration, samples for analysis were prepared by thoroughly mixing 1 mL of the water sample with 9 mL of 100 mg/L Lanthanum solution in a test tube. Samples were then aspirated 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 the water samples were calculated using equation (3.7) below;

$$C_{(Mg^{2+})\ \text{in mg/L}} = C_{(Mg^{2+})\ \text{AAS in mg/L}} \times D_f \qquad (3.7)$$

where,

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

3.4.1.5 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, nebuliser and mixing chamber, simple colour filters (interference type) and photo-detector.

Three (3) standards (20, 50 and 100 mg/L) Na^+ and K^+ mixture were 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 aspiration 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. Samples were then aspirated enough times to secure a reliable average reading.

The concentration of Na^+ or K^+, $C_{(Na^+ or K^+) in mg/L}$ in water samples were calculated using equation (3.8):

$$C_{(Na^+ or K^+) in mg/L} = C_{(Na^+ or K^+)FP in mg/L} \times D_f \qquad (3.8)$$

where,

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

3.4.1.6 Trace metals parameters

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

Prior to trace element determination, water samples were digested on a hot plate for 3 hours in a fume hood[1]. This was done by pipetting 4.5 mL of conc. HCl and 0.5 mL conc. HNO_3 into 40 mL of water samples in a 100 mL borax glass beaker, and placed on a hot plate. After, the 3 hours the digested samples were made to cool, filtered and diluted with double distilled water to make a volume of 30 mL (nominal volume).

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[1] Samples were digested to determine the total trace metal concentration (AAW, 1999).

3.4.1.7 Determination of As by HG-AAS

In other to reduce all As^{5+} to As^{3+}, 4 mL of freshly prepared 5 M KI was added to the digested samples and this is represented by the equation;

$$As^{5+} + 2I^{-} \longrightarrow As^{3+} + I_2 \tag{3.9}$$

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

$$3BH_4^{-} + 3H^{+} + 4H_3AsO_3 \longrightarrow 3H_3BO_3 + 4AsH_3 + 3H_2O \tag{3.10}$$

$$BH_4^{-} + H^{+} + 3H_2O \longrightarrow H_3BO_3 + 4H_2 \tag{3.11}$$

The gaseous AsH_3 and H_2 generated were separated from the liquid phase and transferred with an argon gas flow and dried by a stream of nitrogen gas. The liquid goes to waste and the gaseous hydride and hydrogen were swept out of the vapour generation vessel into the atomisation system of the AAS.

Sub-stock solution (10 mg/L) was by prepared diluting 1 mL of stock solution with distilled water into 100 mL solution. Calibration standards (0.2, 0.4, 0.6, 0.8 and 1.0 mg/L) were prepared by diluting 2, 4, 6, 8 and 10 mL of sub-stock solution with distilled water into 100 mL solution. These were used to calibrate the instrument. Samples were then aspirated into the atomic absorption spectrometer (AAS) and for every 10 readings a standard is aspirated as a quality control measure.

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

$$\text{Final conc. (mg/L)} = \frac{\text{Conc.}_{\text{AAS}} \times \text{D}_{\text{f}} \times \text{Nominal volume}}{\text{Sample volume (mL)}} \tag{3.12}$$

where,

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

3.4.1.8 Determination of Cd, Co, Fe, Ni and Pb using FAAS

Sub-stock solutions of 10 mg/L Cd and 100.0 mg/L of (Co, Fe, Ni, and Pb) were prepared by diluting 1 mL (Cd stock solution) and 10.0 mL (Co, Fe, Ni, and Pb stock solution) with distilled water into 100 mL solutions. Three (3) working standards 0.5, 2, 5 mg/L Cd were prepared by diluting 5, 20 and 30 mL each of Cd sub-stock solution with distilled water into 100 mL solutions.

Three (3) working standards (2, 5, 10 mg/L) each for Co, Fe, Ni, and Pb were prepared from the sub-stock solution of Co, Fe, Ni, and Pb. These were done by diluting 2, 5, 10 mL of each of sub-stock solution with distilled water into 100 mL solutions. This was used to calibrate the instrument.

The digested samples were then aspirated into the atomic absorption spectrometer (AAS) and for every 10 readings a standard is aspirated as a quality control measure.

The concentration of Cd, Co, Fe, Ni and Pb in each water sample read from the AAS were used to calculate for their final concentrations in the water samples according the equation (3.13);

$$\text{Final conc. (mg/L)} = \frac{\text{Conc.}_{\text{AAS}} \times \text{D}_{\text{f}} \times \text{Nominal volume}}{\text{Sample volume(mL)}} \qquad (3.13)$$

where,

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

3.4.2 Stable Isotopes Analyses (δ^2H and δ^{18}O)

The LDR DT-100 liquid water stable isotope analyser was used to determine the δ^2H and δ^{18}O composition of the water samples. The analysis was performed in the Isotope Hydrology laboratory, Ghana Atomic Energy Commission, Ghana. The instrument utilizes an Off-Axis Integrated Cavity Output Spectroscopy (off axis ICOS) via laser absorption approach which can generate optical path lengths of about 2500 meters in a 25 cm cell, to measure absolute abundances of ^{2}HHO, HH^{18}O, and HHO. These approach significantly increase measured absorption and result in a high signal-to-noise ratio for precise isotope measurements (IAEA, 2009).

The equipment is made up of a laser analysis system, an internal computer, CTC LC-PAL liquid autosampler, a small membrane vacuum pump, and a room air intake line that passes air through a Drierite column for moisture removal (Fig. 3.7).

Three secondary standards were used for the analysis: two calibration standards prepared from IAEA reference material, and a control standard ("in-house" prepared).

One millimetre (1mL) automatic pipette with disposable tips was used to pipette 1 mL aliquot of dummy samples, water samples and standards into 1.5 mL labelled autosampler glass vials and were closed with PTFE septum caps. Samples were place in their proper position on the autosampler tray in the following order; (i) 1st position on the tray (top left corner) was the dummy sample. The dummy sample was tap water; (ii) 2nd position was the heavy isotope calibration standard; (iii) 3rd position was the light isotope calibration standard; (iv) 4th position was the third standard (the control standard); and

(v) The next positions were five water samples followed by three standards.

This was repeated till the last set of standards ends the arrangement in the tray. Measurement of each sample lasted for about 25 minutes. After samples analysis, the results were then transfer onto a memory stick for archiving and post-processing. The IAEA spreadsheet was use for post-processing of the results.

3.4.2.1 Calculations of stable isotopes

The stable isotope composition of $\delta^{18}O$ and $\delta^{2}H$ were calculated relative to internal standards that were calibrated using Vienna-Standard Mean Ocean Water (VSMOW) (Coplen, 1996). Post-processing procedure was used to calculate delta-scale values with respect to the Vienna Standard Mean Ocean Water (VSMOW) using the relation;

$$\delta = \frac{R_{measured} - R_{VSMOW}}{R_{VSMOW}} \qquad (3.14)$$

where,

R is $^{2}H/^{1}H$ or $^{18}O/^{16}O$. (IAEA, 2009).

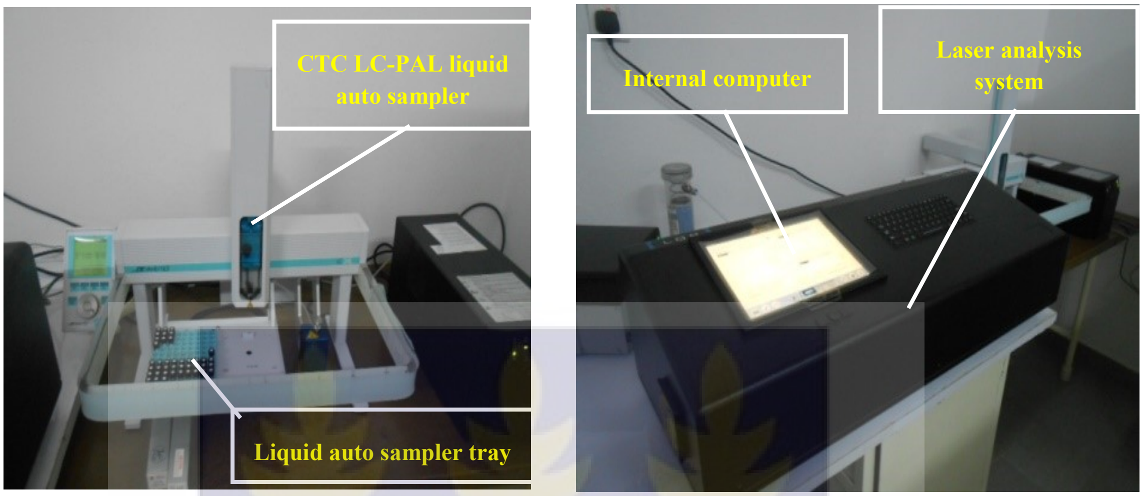

Fig. 3.7: Picture of LDR DT-100 liquid water stable isotope analyser

3.5 METHODS USED IN GEOCHEMICAL DATA ANALYSIS

3.5.1 Bivariate and Piper plots.

The bivariate and Piper plots help provide a better understand the groundwater chemistry, weathering processes and geochemical evolution (Adomako et al., 2010). In general, groundwater chemical evolution model (i.e Piper) reveals groundwater hydrochemical facies in any catchment (Appelo and Postma, 1996a; Edmunds et al., 2003, 2002; Freeze and Cherry, 1979a). The major advantages of the Piper plot is that major analysis can be plotted on the same diagram (Adomako et al., 2010). It can also be used to identify mixing of waters (Appelo and Postma, 1996c). However, the disadvantages of the Piper plot are that concentrations are renormalized, and also it cannot easily accommodate waters where other cations or anions that may be significant (Adomako, 2010). In this study the graphing software used for the bivariate plot and Piper diagram were Microsoft excel software (Office 2013) and Diagrammes software [Roland SIMLER Laboratoire d'Hydrogéologie d'Avignon (version 6.5)] respectively.

3.5.2 Multivariate statistical analyses

Multivariate statistical analyses are statistical techniques and methods which are primarily used to treat data with several variables. The objective is to investigating the dependence relations between the involved variables. Some of the multivariate techniques include Principal Component Analysis (PCA), Factor Analysis (FA), Cluster Analysis (CA) and Discriminant Analysis (DA). These techniques have various applications in chemical and geochemical studies, examples of works that have use these techniques are in (Adomako et al., 2011; Bhuiyan et al., 2011; Fathy et al., 2012; Gromski, 2015; Kumar et al., 2011; Lei, 2013; Osei, 2010; Papazoglou, 1998; Pejman et al., 2009; Wellock, 2006; Zhao and Cui, 2009).

3.5.2.1 Agglomerative Hierarchical Clustering (AHC)

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.

First step, is to compute the Euclidean distance matrix (I × I) considering each individual as a cluster. The Euclidean distance is given by;

$$d^2(i,l) = \sum_{k=1}^{K} \frac{1}{s_k} (x_{ik} - x_{lk})^2 \tag{3.15}$$

where,

x_{ik} denote the value of individual *i* for variable *k*, s_k the standard deviation of variable k for *i* individuals described by *k* quantitative variables (Husson et al., 2011a).

Second step is to merge two clusters A and B which are the closest with respect to the Ward's criterion:

$$d(A,B) = \frac{n_A n_B}{n_A + n_B} d_{A,B}^2 \tag{3.16}$$

where,

d is the euclidean distance, d_{AB}^2 is the distance between the A-th and B-th cluster (Husson et al., 2011a).

3.5.2.2 *Principal Component Analysis (PCA)*

PCA transforms raw data into a new coordinate system by an orthogonal linear transformation. A data matrix **X** of dimension (*I* × *J*), where I is the number of rows (samples) and J is the number of columns (variables), which (*J* >> 1). The method of PCs uses new formal variables $\mathbf{t_a}(a = 1, \ldots\ldots, A)$, which are linear combinations of the original variables $\mathbf{x_j}(j = 1, \ldots\ldots, \mathrm{J})$ that is,

$$\mathbf{t_a} = \mathbf{p_{a1}x_1} + \cdots + \mathbf{p_{aj}x_j} \tag{3.17}$$

$$\mathbf{X} = \mathbf{TP^t} + \mathbf{E} = \sum_{\mathrm{a}=1}^{\mathrm{A}} \mathbf{t}_\mathrm{a}\mathbf{p}_\mathrm{a}^\mathrm{t} + \mathbf{E} \tag{3.18}$$

Matrix **T** is called the scores matrix. It is of the dimension (*I* × *A*). Matrix **P** is called the loadings matrix. It is of the dimension (*J* × *A*). **E** is the residuals matrix of the dimension

($I \times J$). New variables $\mathbf{t}_\mathbf{a}$ are called principal component (PCs) (Pomerantsev, 2014). PCA can be performed using both correlation and covariance matrices (Martinez and Martinez, 2005). However, the correlation matrix is often used for PCA when some variables have variances that are very much greater than the others (Martinez and Martinez, 2005).

To perform PCA, the first step is to compute a correlation matrix and then compute the eigenvectors and eigenvalues from the computed correlation matrix.

The *FactoMineR* package version 1.28 developed by Francois Husson, Julie Josse, Sebastien Lê, and Jeremy Mazet, for Multivariate Exploratory Data Analysis and Data Mining with R, was used to perform principal component analysis and Hierarchical clustering on the principal components (Lê et al., 2008). This package was part of the R statistical software version 3.2.3 (2015-12-10) for windows.

3.5.3 Spatial Analysis

The ArcGIS 10.2 Spatial Analyst software was used to identify patterns within the hydrochemical data. This techniques aid in visualising the spatial continuity and temporal variation of the hydrochemical variables (Sánchez-Martos et al., 2001). In this method hydrochemical data is represented in a surface in a form of x, y that define the location of the sample and the change characteristic (hydrochemical variable) represented by Z. This is done by interpolating hydrochemical data into surfaces. The Inverse Distance Weighted (IDW) interpolation method was employed in this study.

3.5.3.1 Inverse Distance Weighted (IDW) interpolation

The IDW determines cell values using a linear-weighted combination set of sample points (Childs, 2004). The weight assigned is a function of the distance of an input point from the output cell location. Hence, the greater the distance, the less influence the cell has on the output value (Childs, 2004).

3.6 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) MEASURES

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

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).

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

(i) All glassware and sampling containers were soaked in nitric acid (10 % HNO_3) for three (3) days and rinsed with deionized water before use. This was to ensure that the sample bottles were free from contamination, which could affect the concentrations of various ions in the water samples.

(ii) Boreholes were purged for ten minutes to flush the stagnant water retained in pipes. In the case of hand-dug wells, it was properly checked and confirmed that the dug well was constantly used. This was to ensure that stale and stagnant water was not sampled.

(iii) Surface water samples (Anayari River and Irrigation Dams) collected at least about 10 m away from it banks.

(iv) Water samples collected, were provided with an identification label on which the following information were legibly and indelibly 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% were relied on for subsequent interpretation.

3.6.1 Determination of Charged-Balance Error (CBE) groundwater

The fundamental condition of electrolyte solutions on macroscopic scale is that such solutions are electrically neutral (Freeze and Cherry, 1979b). This means that in groundwater, the total sum of the positive charges (cations, in meq/L) must be equal to the sum of all the negative charges (anions, in meq/L). However, analytical errors and unanalysed constituents in the chemical analyses cause electrical imbalances. A measurement of this imbalance is the charge-balance error (CBE), and is used to verify the validity and quality of water analyses. CBE was calculated using equation (3.19)

$$\mathrm{CBE} = \frac{\sum \mathrm{cations} - \sum \mathrm{anions}}{\sum \mathrm{cations} + \sum \mathrm{anions}} \times 100\% \qquad (3.19)$$

A positive CBE indicates that one or more of the cations was over determined, or one or more of the anions was under-determined, or both. Contrariwise, negative CBE indicates that one or more of the cations was under-determined, or nor or more of the anions was over-determined, or both. CBE within ± 5% are acceptable water analyses (Freeze and Cherry, 1979b). The CBE analyses of groundwater samples in the study area were within ± 5 % (Appendix A. 1).

CHAPTER FOUR

4.0 RESULT AND DISCUSSION

This chapter deals with the interpretation of groundwater chemistry, stable isotope ($\delta^{2}H$ and $\delta^{18}O$) content in surface, hand-dug well as well as the boreholes in the study area. Additionally, all the data obtained from the studies will also be discussed.

4.1 PHYSICO-CHEMICAL PARAMETERS

The results for the physico-chemical parameters (pH, Salinity, Temperature, Electrical conductivity [EC] and Total dissolved solid [TDS]) determined in water samples (groundwater and surface water) from the study area are presented (Table 4.1 and Table 4.2) respectively.

4.1.1 pH of Groundwater and Surface water

The pH values obtained for both groundwater and surface water are shown in Table 4.1 and Table 4.2 respectively. Both the groundwater and surface water sampled from the study area were near neutral to near alkaline. The pH of the groundwater ranged from 6.30 to 7.40; whilst the surface water ranged from 6.9 to 7.8. The groundwater samples recorded the lowest pH value at PUB1 while the highest pH was found at MAB35. The pH values seems to agree with pH values of groundwater in granitic environment as indicated in the earlier works done in the study area, (Akiti, 1980, 1982; Martin, 2006; Pelig-Ba, 1998).

However, groundwaters which are slightly alkaline in granitic environment may be due to the dissolution of silicate and carbonates minerals (Pelig-Ba, 1987). This is illustrated by equations below;

$$CaCO_{3(s)} + CO_2 + H_2O \longrightarrow Ca^{2+} + 2HCO_3^- \qquad (4.1)$$

$$CaAl_2Si_2O_{8(s)} + 2H^+ \longrightarrow Ca^{2+} + H_2O + Al_2Si_2O_5(OH)_{4(s)} \qquad (4.2)$$

$$NaAlSiO_{8(s)} + 2CO_2 + 6H_2O \longrightarrow Al_4Si_4O_{10}(OH)_{2(s)} + 2Na^+ + 2HCO_3^- + 2H_4SiO_4 \qquad (4.3)$$

In general, pH of natural waters are controlled by reactions involving the consumption of hydrogen and hydroxyl ions, such reaction are; biological processes, reduction/oxidation reactions and dissolution/precipitation (Hill, 2000). Each reaction however, depends upon factors such as the geology, the solubility of the bedrock, soil type and temperature (Hill, 2000).

Table 4.1: Physico-chemical, Chemical (mg/L) and isotopic composition (δ ‰/VSMOW) of groundwater samples

Site ID	**Temp** *°C*	**pH**	**EC** *µS/cm*	**TDS** *mg/L*	**Sal** *‰*	**HCO_3^-**	**Na^+**	**K+**	**Ca^{2+}**	**Mg^{2+}**	**F^-**	**Cl^-**	**NO_3^-**	**PO_4^{3-}**	**SO_4^{2-}**	**$\delta^{18}O$** [‰]	**δ^2H** [‰]
PUB1	31.8	6.3	387	193	0.1	205.0	65.0	7.70	27.2	1.83	0.278	42.49	4.640	<0.001	0.003	-3.72	-20.85
PUB2	31.2	6.6	313	156	0.1	258.6	59.9	5.00	40.0	1.29	0.021	12.02	0.026	0.471	4.056	-3.92	-21.95
PAB3	32.5	6.7	672	335	0.3	351.4	66.8	18.1	59.2	5.34	0.002	19.84	20.64	0.002	23.19	-3.76	-21.95
PAB4	33.9	6.9	506	253	0.2	200.1	46.4	9.40	19.2	5.97	0.368	10.07	0.021	1.046	8.697	-3.93	-24.20
PAB5	33.6	6.6	511	256	0.2	244.0	46.0	9.10	32.0	5.39	0.002	5.805	24.25	<0.001	6.436	-4.35	-23.75
BAB6	34.5	6.4	450	225	0.1	287.9	60.8	9.10	40.0	2.35	0.725	6.996	30.19	<0.001	5.316	-3.29	-19.40
BOB8	35.0	7.1	457	228	0.1	283.0	60.6	7.00	32.0	3.23	0.398	2.904	3.979	0.001	6.070	-3.39	-22.70
BOB10	32.3	6.7	450	225	0.1	512.4	168	12.1	40.0	2.8	0.035	32.93	0.012	0.209	2.093	-3.47	-22.80
NAB12	31.3	6.8	335	168	0.1	263.5	57.5	8.90	32.0	2.76	1.469	6.268	11.21	<0.001	3.910	-4.03	-22.50
NAB13	32.9	6.8	506	253	0.2	185.4	37.1	7.40	38.4	3.79	2.174	19.77	27.64	0.265	16.02	-3.53	-22.75
NAB14	31.3	6.7	232	116	0.0	92.72	18.7	13.8	17.6	0.95	1.600	16.13	22.06	1.766	0.063	-4.20	-25.65
SAB16	31.7	7.1	388	194	0.1	190.3	42.4	8.50	35.2	1.95	0.586	3.364	26.01	0.012	32.46	-4.23	-22.20
PAB19	30.8	6.8	479	239	0.2	244.0	50.5	8.70	40.8	3.78	0.241	17.60	27.86	0.027	13.59	-3.65	-19.40
BUB20	31.5	6.7	331	165	0.1	180.6	36.9	8.10	36.8	0.99	1.171	16.29	34.29	0.018	5.370	-3.96	-22.90
BKB22	32.4	6.8	321	160	0.1	214.7	50.4	9.30	28.8	1.68	0.179	12.79	29.29	1.552	3.063	-3.52	-21.80
BKB23	32.4	6.6	358	178	0.1	273.3	56.6	9.90	35.2	1.45	2.069	5.724	10.40	0.024	8.671	0.62	-4.200
NTB26	32.0	7.1	363	182	0.1	190.3	48.5	7.80	28.8	1.59	0.035	30.16	0.947	1.039	2.189	-3.58	-17.95
NTB27	31.5	6.8	352	176	0.1	341.6	82.1	6.00	35.2	0.99	0.001	11.78	0.004	0.010	0.002	-4.07	-22.95
NTB29	33.1	6.7	350	175	0.1	234.2	65.1	5.00	30.4	1.80	0.105	36.05	1.048	0.295	2.179	-3.95	-22.15
TBB30	31.9	7.1	308	154	0.1	200.1	47.5	7.00	28.8	1.57	0.213	23.80	1.047	2.552	3.682	-4.10	-22.50
TBB31	32.2	7.3	424	212	0.1	219.6	58.1	12.2	42.4	2.42	0.036	37.92	27.01	0.149	1.989	-4.32	-23.60
TBB32	32.6	6.9	230	115	0.0	146.4	39.9	6.10	17.6	1.23	0.172	19.49	2.011	0.523	1.903	-4.17	-21.50
MAB33	32.6	7.3	327	163	0.1	273.3	61.9	1.30	35.2	1.98	0.557	5.478	19.45	<0.001	2.230	-3.56	-18.20
MAB34	32.2	7.1	335	168	0.1	200.1	39.0	2.80	30.4	2.36	0.185	5.367	12.62	0.003	4.775	-3.58	-20.80
MAB35	32.3	7.4	452	226	0.1	244.0	47.8	10.5	34.4	3.81	0.153	21.05	2.064	0.024	1.635	-3.23	-19.00

GOB36	31.3	6.9	458	229	0.1	270.8	62.8	9.10	42.4	2.2	0.544	33.26	0.031	0.013	3.481	-3.48	-20.10
GOB37	30.4	7.2	473	237	0.2	331.8	73.0	10.9	38.4	2.23	0.660	8.212	9.518	<0.001	9.310	-3.56	-21.20
GOB38	31.2	7.0	386	193	0.1	239.1	56.6	9.00	32.8	2.36	<0.001	21.08	2.263	0.026	4.711	-3.82	-21.60
MWB42	32.4	6.8	679	340	0.3	409.9	97.3	13.1	52.8	3.84	1.294	34.03	0.549	0.089	3.205	-3.03	-19.40
MWB43	32.1	6.9	470	235	0.1	268.4	62.6	8.10	34.4	3.82	2.391	15.36	26.23	0.152	6.488	-2.54	-16.20
MTB44	32.6	7.1	426	213	0.1	370.9	116	10.3	35.2	3.01	0.110	29.84	6.943	1.094	7.040	-3.15	-22.05
MNB45	32.4	6.9	472	236	0.2	278.2	65.9	5.80	33.6	3.4	0.134	9.077	7.149	0.003	2.130	-2.15	-15.20
MNB46	32.2	6.8	511	255	0.2	287.9	71.9	6.80	43.2	2.94	0.182	28.09	2.049	1.095	2.438	-3.36	-22.30
MKB47	32.1	6.8	464	232	0.1	336.7	63.8	4.70	57.6	1.95	0.020	14.74	33.18	1.004	1.390	-3.38	-18.85
MKB48	32.6	7.0	428	215	0.1	283.0	67.4	10.6	38.4	1.61	0.172	18.90	31.94	0.083	0.984	-2.63	-17.90
MHB49	32.6	7.1	734	368	0.3	488.0	119	15.1	44.0	3.94	1.320	0.639	38.86	0.011	0.379	-3.75	-18.90
MSB50	32.5	7.3	564	283	0.2	258.6	82.0	10.6	21.6	3.64	0.138	34.93	0.389	1.035	1.503	-4.08	-22.50
BOW9	31.4	6.8	308	154	0.1	165.9	41.7	3.90	30.4	1.36	0.287	9.848	36.46	0.003	10.41	-3.47	-18.70
PAW18	30.3	6.7	535	267	0.2	278.2	82.1	3.50	36.8	3.49	0.825	25.18	8.503	<0.001	6.750	-3.94	-17.90
BUW21	29.5	6.7	441	221	0.1	258.6	59.3	17.1	44.0	0.72	0.045	8.084	19.27	0.013	17.29	-3.96	-18.70
PUW40	29.7	7.0	348	174	0.1	156.2	42.9	19.1	36.0	0.88	1.039	43.05	1.321	0.830	3.928	-3.59	-16.55
Mini	**29.5**	**6.3**	**230**	**115**	**0.0**	**92.72**	**18.7**	**1.30**	**17.6**	**0.72**	**0.001**	**0.639**	**0.004**	**0.001**	**0.002**	**-4.35**	**-25.65**
Max	**35.0**	**7.4**	**734**	**368**	**0.3**	**512.4**	**168**	**19.1**	**59.2**	**5.97**	**2.391**	**43.05**	**38.86**	**2.552**	**32.46**	**0.62**	**-4.200**
Mean			**428**	**214**	**0.1**	**261.4**	**62.88**	**8.99**	**35.6**	**2.55**	**0.55**	**18.45**	**13.74**	**0.450**	**5.880**	**-3.51**	**-20.64**

EC (Electrical conductivity), **TDS** (Total Dissolved Solid), **Temp** (Temperature), **Sal** (Salinity), **Min** (Minimum), **Max** (Maximum)

Table 4.2: Physico-chemical, chemical (mg/L) and isotopic composition (δ ‰VSMOW) of surface water in the study area

Site ID	**Temp °C**	**pH**	**EC µS/cm**	**TDS mg/L**	**Sal ‰**	**HCO_3^-**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**F^-**	**Cl^-**	**NO_3^-**	**PO_4^{3-}**	**SO_4^{2-}**	**$\delta^{18}O$ [‰]**	**δ^2H [‰]**
NAD15	34.6	7.8	94.50	47.0	0.0	146.4	41.7	8.10	17.6	0.160	0.011	9.038	2.535	0.032	7.724	-3.44	-15.95
BOS17	33.5	7.5	63.80	32.0	0.0	24.40	8.10	10.4	4.80	0.030	0.013	6.479	16.10	1.004	3.858	-3.32	-18.00
BKS24	33.3	7.1	64.40	31.0	0.0	43.92	11.2	10.1	9.60	0.020	0.009	12.05	2.310	1.935	3.938	-2.43	-12.60
NTS28	32.6	7.6	48.10	24.0	0.0	29.28	9.20	8.50	6.40	0.009	0.031	3.533	0.757	0.021	12.69	-3.07	-16.60
BAS7	34.6	6.9	92.60	46.0	0.0	73.20	20.5	7.00	9.60	0.280	0.014	8.711	0.586	<0.001	3.072	-2.96	-13.20
BOS11	32.6	7.2	85.70	43.0	0.0	78.08	16.8	5.00	9.60	0.400	0.355	0.778	2.807	0.205	1.571	-3.66	-18.70
BKS25	33.0	7.5	99.60	50.0	0.0	58.56	17.5	4.90	9.60	0.240	0.023	13.99	0.080	0.324	1.935	-3.11	-17.40
PUS39	26.8	7.5	77.20	39.0	0.0	58.56	14.6	3.40	12.0	0.340	0.001	14.50	0.003	<0.001	0.036	-2.66	-10.53
DOS41	28.4	7.8	54.70	28.0	0.0	39.04	11.4	5.10	8.80	0.110	0.134	11.29	0.960	0.528	2.943	-3.73	-17.90
MIS51	31.1	7.4	69.10	34.0	0.0	39.04	14.3	5.50	3.20	0.680	0.013	9.378	4.922	1.098	0.389	-3.38	-17.60
Min	**26.8**	**6.9**	**48.10**	**24.0**	**0.0**	**24.40**	**8.10**	**3.40**	**3.20**	**0.009**	**0.001**	**0.778**	**0.003**	**0.021**	**0.036**	**-3.73**	**-18.70**
Max	**34.6**	**7.8**	**99.60**	**50.0**	**0.0**	**146.4**	**41.70**	**10.4**	**17.6**	**0.680**	**0.355**	**14.50**	**16.10**	**1.935**	**12.69**	**-2.43**	**-10.53**
Mean			**74.97**	**37.4**	**0.0**	**59.05**	**16.53**	**6.80**	**9.12**	**0.227**	**0.060**	**8.973**	**3.105**	**0.643**	**3.815**	**-3.18**	**-15.85**

EC (Electrical conductivity), **TDS** (Total Dissolved Solid), **Temp** (Temperature), **Sal** (Salinity), **Min** (Minimum), **Max** (Maximum)

4.1.2 Temperature of Groundwater and Surface water

Temperatures for the groundwater varied from 29.5 to 35 ºC with a mean value of 32.1 ºC (Table 4.1), whilst that for surface water varied between 26.8 to 34.6 ºC with a mean value of 32.1 ºC (Table 4.2). The variations in temperature can be attributed to several factors such as different sampling time, the season and also, the flow and well depth (Chapman and Kimstash, 1996).

4.1.3 Electrical conductivity (EC) and Total Dissolved Solids (TDS)

4.1.3.1 Groundwater

Electrical conductivity (EC) and Total dissolved solid (TDS) values obtained for the groundwater samples ranged from 230 µS/cm to 734 µS/cm and 115 mg/L to 368 mg/L respectively (Table 4.1). In general, values for the total dissolved solid in the study area were low and seems to relate to observed TDS values in silicates rocks (Appelo and Postma, 1996d). The values of the groundwater increased outwardly and strongly from the centre of the catchment along the flow gradients within the aquifer to the North western and South eastern portions of the study area (Fig. 4.1). The TDS also showed a similar trend. Normally, low EC and TDS values are associated with recharge areas, while high EC and TDS values are associated with discharge area (Freeze and Cherry, 1979a). In general, the TDS values obtained for groundwater in the study area were < 1000 mg/L indicating that they are fresh water (Drever, 1982a).

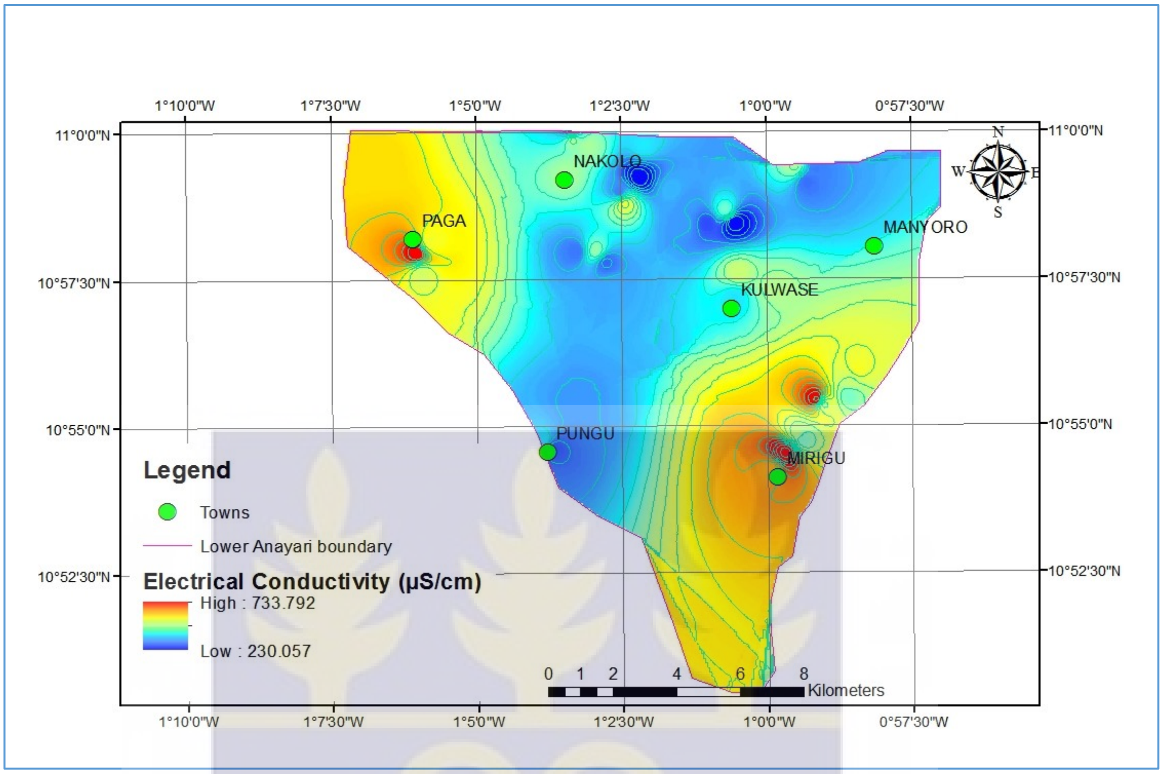

Fig. 4.1: Spatial distribution of Electrical Conductivity (µS/cm) of groundwater in the study area.

4.1.3.2 Surface water

The EC and TDS values for surface water were generally low compared to that of groundwater. They ranged from 48.1 µS/cm to 99.6 µS/cm, and 24.0 mg/L to 50.0 mg/L respectively. The lower electrical conductivities and total dissolved solids (TDS) obtained for surface water the in the study area, may be due to the flow and dynamics of the surface water.

4.2 MAJOR ION CHEMISTRY

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

4.2.1 Major ions

In terms of cations (Table 4.1) Na^+ level in the groundwater was highest ranging from 18.4 mg/L to 168 mg/L with an average of 62.9 mg/L. The level of K^+ ranged from 1.30 mg/L to 19.1 mg/L with an average of 18.9 mg/L. The level of Ca^{2+} ranged from 17.6 mg/L to 59.2 mg/L with an average of 35.6 mg/L. The levels of Mg^{2+} ranged from 0.72 mg/L to 5.97 mg/L with mean of 2.55 mg/L. Averagely, Mg^{2+} concentration in groundwater sampled in the study area was observed to be the least among the major cations. This may be due to the possible montmorillonite ($Na_{0.5}Al_{1.5}Mg_{0.5}Si_4O_{10}(OH)_2$) formation as water reacts with albite ($NaAlSi_3O_8$) under neutral or alkaline conditions (Appelo and Postma, 1996d; Garrels, 1975). This is illustrated by equation (4.4);

$$3NaAlSi_3O_8 + Mg^{2+} + 4H_2O \longrightarrow 2Na_{0.5}Al_{1.5}Mg_{0.5}Si_4O_{10}(OH)_2 + 2Na^+ + H_2SiO_4 \tag{4.4}$$

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[2] CO_2 dissolves in water to form carbonic acid, this reacts with minerals. Thus drives mineral dissolution.

The trend of the levels of major cations were $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$.

The level of HCO_3^- ions in the samples showed wide variations ranging from 92.7 mg/L to 512 mg/L with a mean of 261 mg/L. The level of Cl^- ions in groundwater samples ranged from 0.64 mg/L to 43.1 mg/L with a mean of 18.5 mg/L.

The HCO_3^- ion was observed to be the dominant ion in all the samples. This may be due to enriched biogenic CO_2 in rainwater in the soil zone which aggressively might have reacted with silicate minerals in the study area. This illustrated by equation (4.5);

$$NaAlSiO_{8(s)} + 2CO_2 + 6H_2O \longrightarrow Al_4Si_4O_{10}(OH)_2 + 2Na^+ + 2HCO_3^- + 2H_4SiO_4 \qquad (4.5)$$

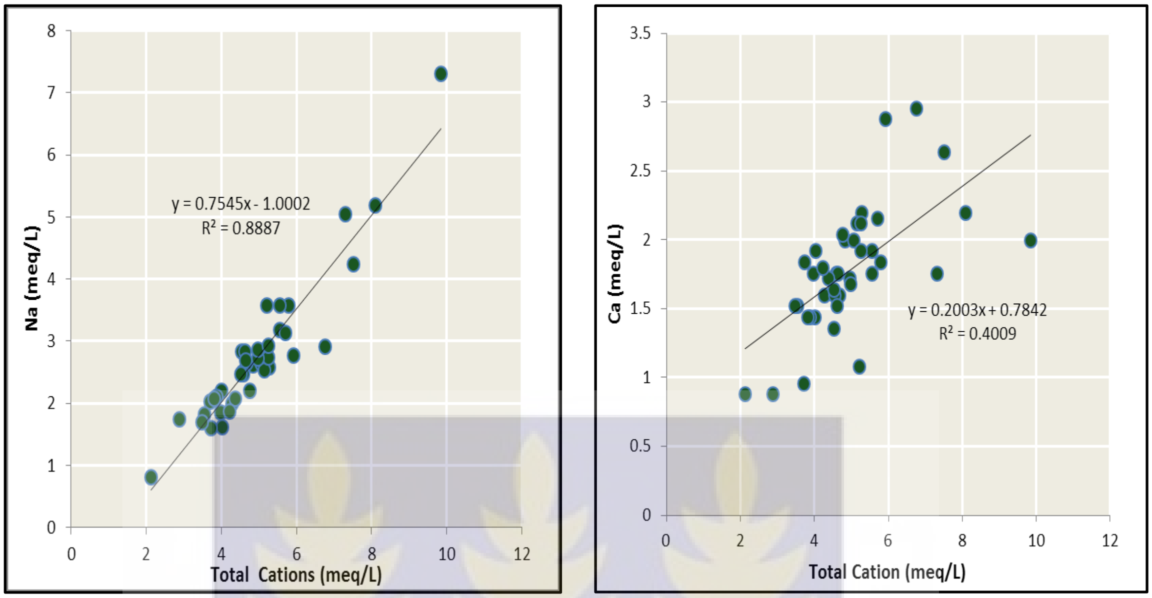
The levels of NO_3^- ions in the groundwater samples were slightly higher than that of SO_4^{2-}. Generally, NO_3^- ions concentrations in excess of 5 mg/L are associated to pollution by human and animal waste, or fertiliser run-off (Chapman and Kimstash, 1996; Younie et al., 1996). More so, SO_4^{2-} is known to arise from the atmospheric deposition of oceanic aerosols and the leaching of sulphur compounds, either sulphate minerals such as gypsum or sulphide minerals such as pyrite, epsomite, mirabillite, from sedimentary rocks (Appelo and Postma, 1996a, 1996b; Benedict et al., 2003; Chapman and Kimstash, 1996). However, the study area is primarily underlain by granitic rocks; although, some granitic rocks may host sulphite minerals such as pyrite. The concentration of SO_4^{2-} where found to be low indicating absence or few sulphide minerals present in the study area. Hence, this may be a reason for increase NO_3^- ions concentrations over SO_4^{2-}.

The NO_3^- ions concentration ranged from 0.004 mg/L to 38.7 mg/L with an average value of 13.7 mg/L. The SO_4^{2-} ions concentration ranged from 0.002 mg/L to 32.7 mg/L with an average of 5.88 mg/L. The trend of dominant major anions concentration were $HCO_3^- > Cl^- > NO_3^- > SO_4^{2-}$.

The levels of F^- and PO_4^{3-} ions concentration in the groundwater were low, and ranged from <0.001 mg/L to 2.39 mg/L, and <0.001 mg/L to 2.55 mg/L respectively (Table 4.1).

4.3 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. Fig. 4.2 shows the plot of the sum of cations ($\sum$ cations) versus Na^+ and Ca^{2+} respectively.



(a) (b)

Fig. 4.2 Graph showing (a) Total cations against Na (b) Total cations against Ca

From Fig. 4.2(a), the Na^+ ions is well correlated with the total cations which may imply that sodium based mineral, probably Na-plagioclase may be present[3]. In addition, all the groundwater samples, had $Na^+/[Na^+ + Cl^-]$ ratio (greater than 0.6) which may indicate that sodium sources are mainly from cation exchange and incongruent dissolution of alumino-silicate (Na-plagioclase or albite) (Adomako, 2010). However, in Fig. 4.2b the total cation versus Ca^{2+} did not show good relation with $R^2 = 0.40$. This may also confirm that the Na^+ ions are dominant over the Ca^{2+} ions in the study area.

The HCO_3^- versus (Ca^{2+}+ Mg^{2+}) was also plotted as shown in Fig. 4.3. The data was observed to fall below the equiline (1:1), this suggest that excess alkalinity in the water has been balanced by the alkalis metals ($Na^+ + K^+$).

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[3] Granite rocks in study area are dominated by feldspar especially plagioclase (Pelig-Ba, 2012)

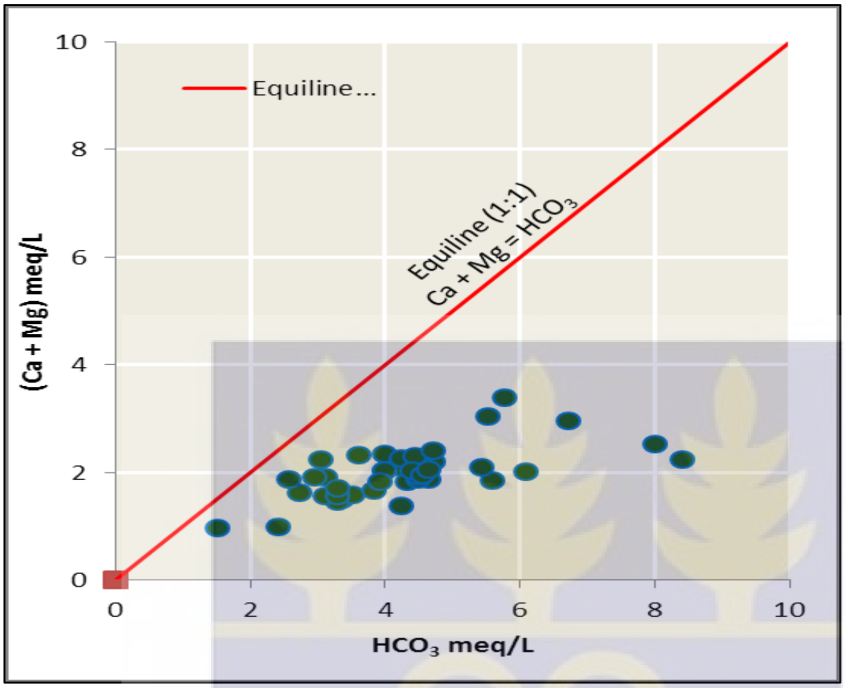

Fig. 4.3: Plot of HCO_3^- versus (Ca^{2+}+ Mg^{2+}) in meq/L

Also, a plot of total cations versus (Na^+ + K^+) [Fig. 4.4] was used to further assess the contribution of cations by silicate weathering. From the Scatter plot of total cations versus (Na + K) [Fig 4.4] all the groundwater data point were below the equiline (1:1), a few along the (Na + K) = 0.5(Total Cations) line and majority falling between the two lines. This gives the indication of these cations are from silicate weathering (Glover, 2013).

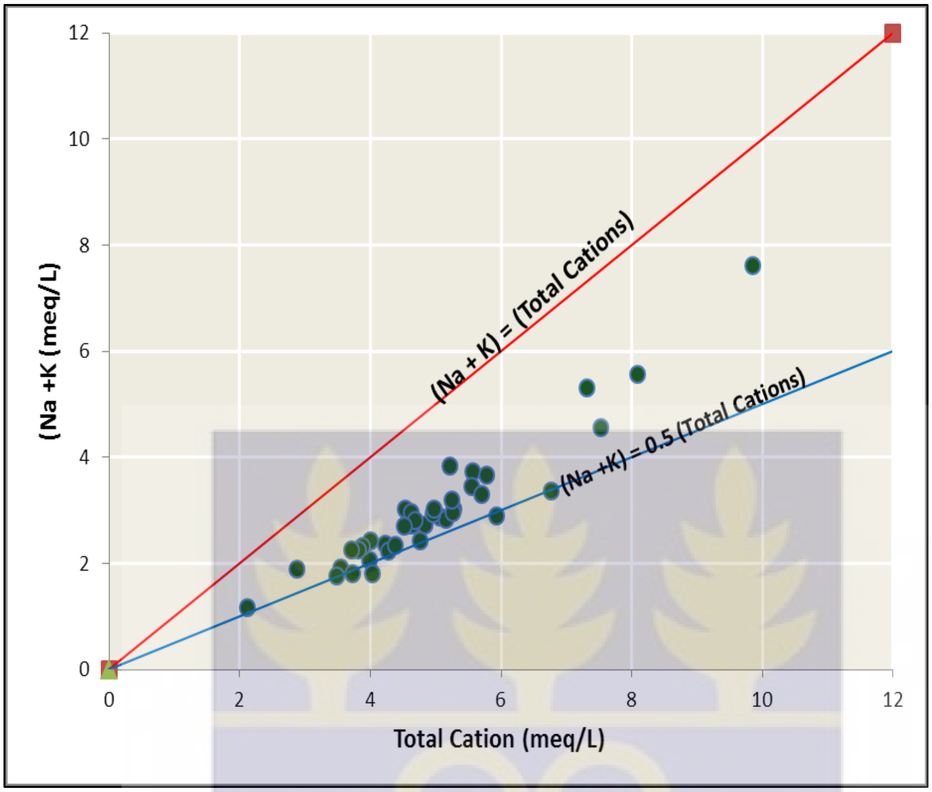

Fig. 4.4: Plot of Total cation versus ($Na^+ + K^+$)

The Na^+/Cl^+ ratio of groundwater ranged from 1.54 to 285; the high Na^+/Cl^+ ratios of groundwater may be explained by Na being derived predominantly from the weathering of plagioclase (Cartwright et al., 2004) represented by the equation below;

$$10Na_{0.6}Ca_{0.4}Al_{1.4}Si_{2.6}O_8 + 31H_2O + 14H_2CO_3 = 7Al_2Si_2O_5(OH)_4 + 6Na^+ + 4Ca^{2+} + 14HCO_3^- + 12H_4SiO_4 \quad (4.6)$$

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. 4.5). 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 2 to 37, this supports that Ca^{2+} and Mg^{2+} ions may have resulted from incongruent dissolution of silicate minerals.

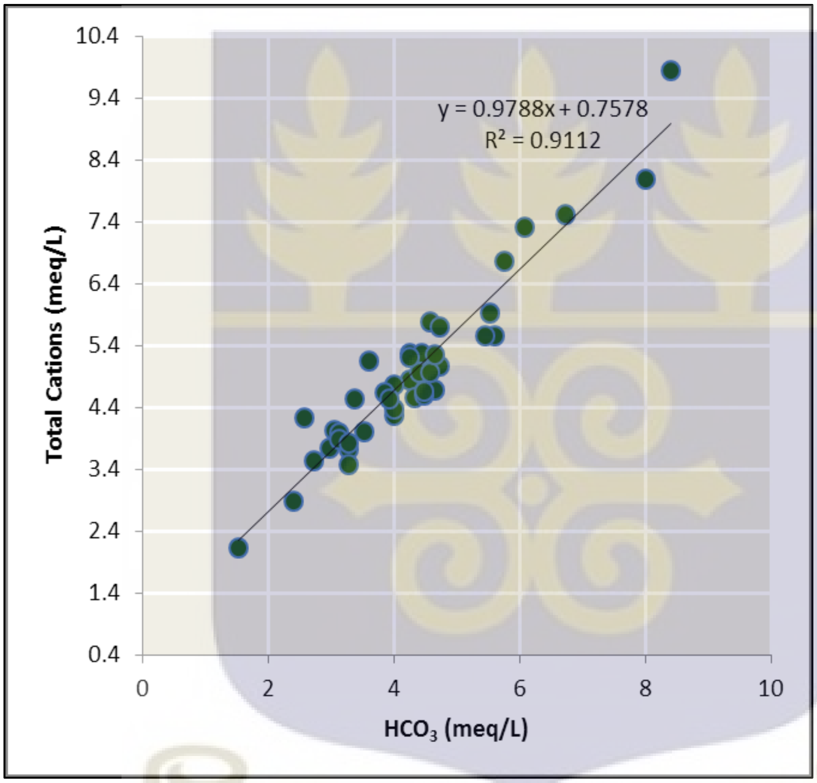

Fig. 4.5: Plot of HCO_3^- versus Total cations

However, argillaceous rocks and organic matter can adsorb H^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} ions in an ion exchange processes and is responsible for the concentration of ions in groundwater. Schoeller, (1965) proposed chloro-alkaline indices 1 and 2 (*CAI*1 and *CAI*2) to understand the ion exchange between the groundwater and its host environment. The chloro-alkaline indices are expressed by the equations shown below:

$$CAI1 = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \tag{4.7}$$

$$CAI2 = \frac{Cl^- - (Na^+ + K^+)}{SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-} \tag{4.8}$$

In the equation above, when there is an exchange between Ca^{2+} or Mg^{2+} in the groundwater with Na^+ and K^+ in the aquifer material, both the above indices are negative, and if there is a reverse ion exchange, then both these indices will be positive.

The chloro-alkaline indices calculated for the groundwater samples in the catchment were all negative, which strongly suggest ion exchange reaction mainly the exchange between Ca^{2+} or Mg^{2+} in the groundwater with Na^+ and K^+ in the aquifer material (Appendix A. 3).

To further test for the possibility that cation exchange reaction significantly affects groundwater composition a plot of $[(Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-})]$ as a function of $(Na^+ - Cl^-)$ were examined (Fig. 4.6). $(Na^+ - Cl^-)$ represents the amount of Na^+ gained or lost relative to that provided by chloride salt dissolution (mostly halite dissolution), while $[(Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-})]$ represents the amount of Ca^{2+} and Mg^{2+} gained or lost relative to that provided by gypsum, calcite and dolomite dissolution. If these processes are significant controlling processes, the relationship between these two parameters should be linear with a slope of -1 (Gibrilla et al., 2010b). Data plots were close to a straight line ($R^2 = 0.96$) with the slopes of -0.99 indicating that Na^+, Ca^{2+} and Mg^{2+} participate in the ion exchange reaction (Fig. 4.6).

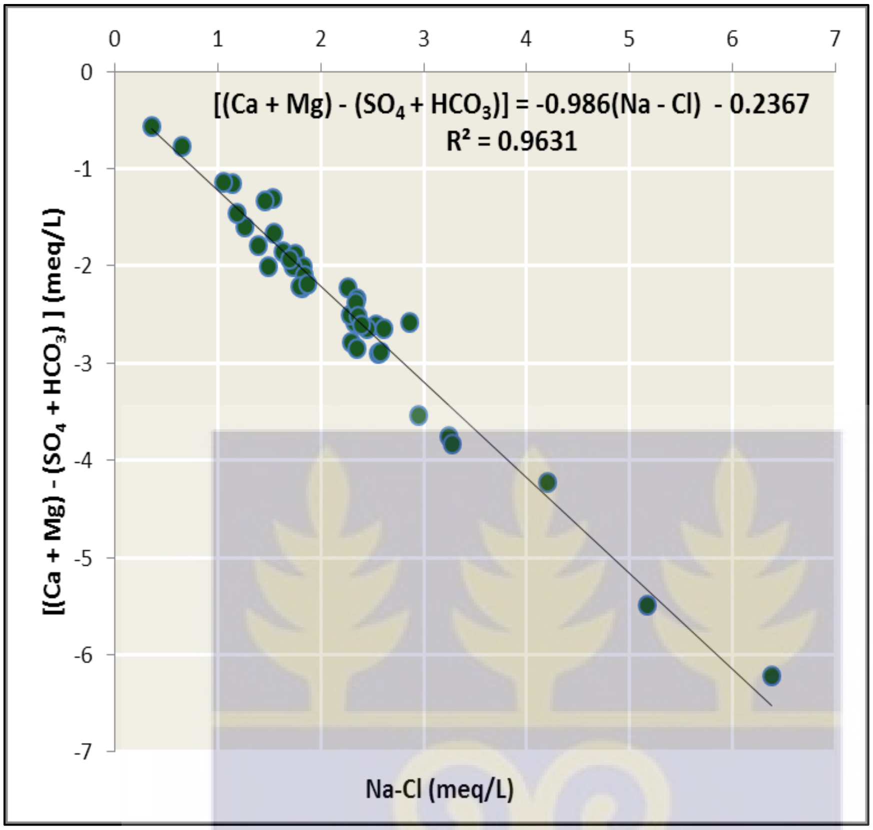

Fig. 4.6: Plot of [(Ca^{2+} + Mg^{2+}) - (SO_4^{2-} - HCO_3^-)] versus (Na^+- Cl^-).

4.4 STATISTICAL ANALYSIS

The R Statistical Software Version 3.2.3 (2015-12-10) for Windows was used to perform Principal Component, and Hierarchical Cluster Analysis to support the conventional hydrochemical technique. The *FactoMineR* package version 1.28 (developed by Francois Husson, Julie Josse, Sebastien Le, and Jeremy Mazet, for Multivariate Exploratory Data Analysis and Data Mining with R), was used to perform Principal Component Analysis and Hierarchical Clustering on the Principal Components (Lê et al., 2008).

The Ward's method of Hierarchical clustering was used. Prior to clustering analysis, principal component analysis was performed on the hydrochemical dataset of groundwater samples using the PCA function of the package. The number of components retained were the principal components whose eigenvalues were above one (Husson et al., 2011b).

4.4.1 Principal Component Analysis (PCA)

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

$$z_{i.j} = \frac{d_{i,j}-\overline{d_i}}{s_i} \tag{4.9}$$

where,

$\overline{d_i}$ and s_i are the mean and standard deviation of all $d_{i,j}\, j = 1, n$. With this transformation, the mean each transformed variable is zero and standard deviation is 1

(Drever, 1982b). In this study, five (5) principal components explain about 81.1% of explained variance of the dataset (Table 4.3).

Table 4.3: Principal Components obtained from hydrochemical data

Principal components	Eigenvalue	Percentage of variance	Cumulative percentage of variance
1	**4.28**	**35.7**	**35.7**
2	**1.80**	**15.0**	**50.7**
3	**1.44**	**12.0**	**62.7**
4	**1.16**	**9.67**	**72.4**
5	**1.05**	**8.73**	**81.1**
6	0.80	6.67	87.8
7	0.58	4.85	92.6
8	0.44	3.66	96.3
9	0.30	2.50	98.8
10	0.13	1.07	99.8
11	0.02	0.17	100

Varimax rotation was performed and hydrochemical variables that were correlated to the principal components (dimensions) at 98% confidence interval were used to characterise the five (5) principal components or dimensions (Table 4.4).

Table 4.4: Hydrochemical variable correlations to principal components (dimensions) and associated significance

Component 1			Component 2		
Variable	Correlation	P-value	Variable	Correlation	P-value
EC	0.94	4.16×10^{-20}	NO_3^-	0.70	3.32×10^{-07}
TDS	0.94	4.69×10^{-20}	SO_4^{2-}	0.58	6.98×10^{-05}
HCO_3^-	0.87	1.99×10^{-13}	Na^+	-0.45	3.49×10^{-03}
Na^+	0.76	7.99×10^{-09}	Cl^-	-0.56	1.24×10^{-04}
Mg^{2+}	0.72	9.21×10^{-08}			
Ca^{2+}	0.66	3.13×10^{-06}			

Component 3			Component 4		
Variable	Correlation	P-value	Variable	Correlation	P-value
Ca^{2+}	0.50	8.13×10^{-04}	K^+	0.55	2.09×10^{-04}
K^+	0.43	4.66×10^{-03}	Cl^-	0.53	3.43×10^{-04}
NO_3^-	0.43	5.00×10^{-03}			
Temp	-0.71	2.18×10^{-07}			

Component 5		
Variable	Correlation	P-value
pH	0.83	1.39×10^{-11}

4.4.2 Cluster Analysis

Hierarchical Cluster Analysis (HCA) was performed in R-mode and Q-mode, the Wards method was applied and Euclidean metric was used as a measure of similarity. The cluster revealed two distinct groups or clusters (Fig. 4.7). The different clusters and their members were extracted as follows: cluster one includes pH, SO_4^{2-}, Cl^-, NO_3^-, while cluster two includes Ca^{2+}, Na^+, HCO_3, K^+, Temperature, Mg^{2+}, EC and TDS. These clusters were used in grouping the groundwater in the study area.

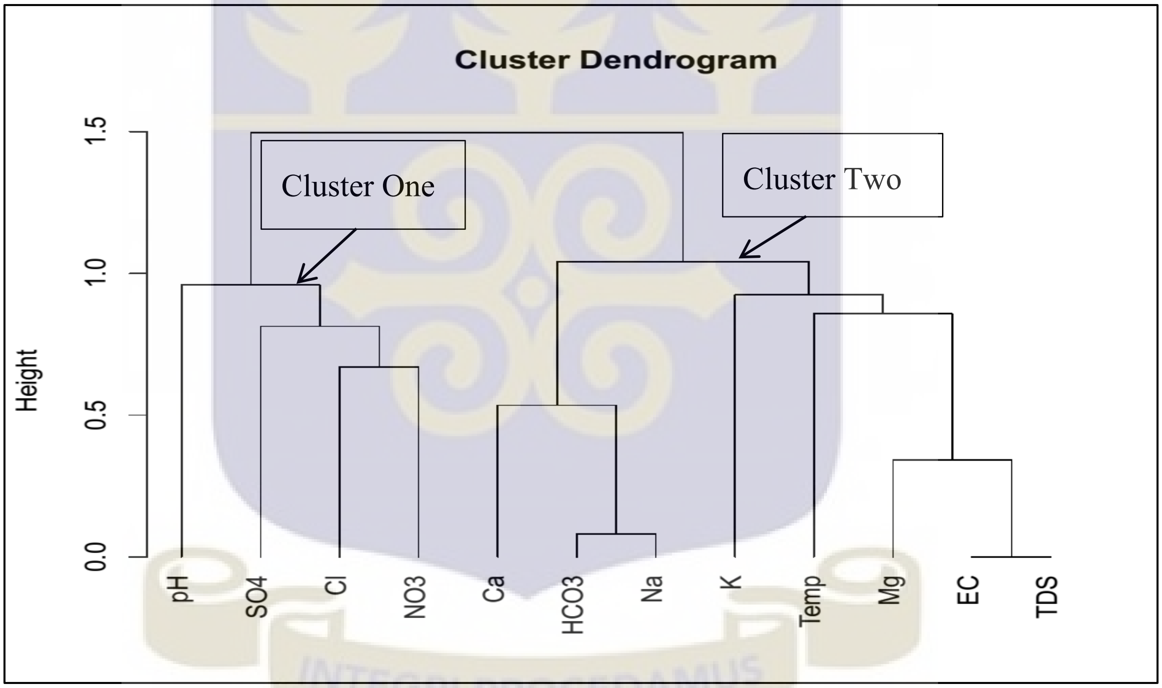

Fig. 4.7: Tree diagram for 12 variables measured for the geochemical studies

Results of cluster analysis by groundwater samples on principal component analysis are represented in a dendrogram (Fig. 4.8).

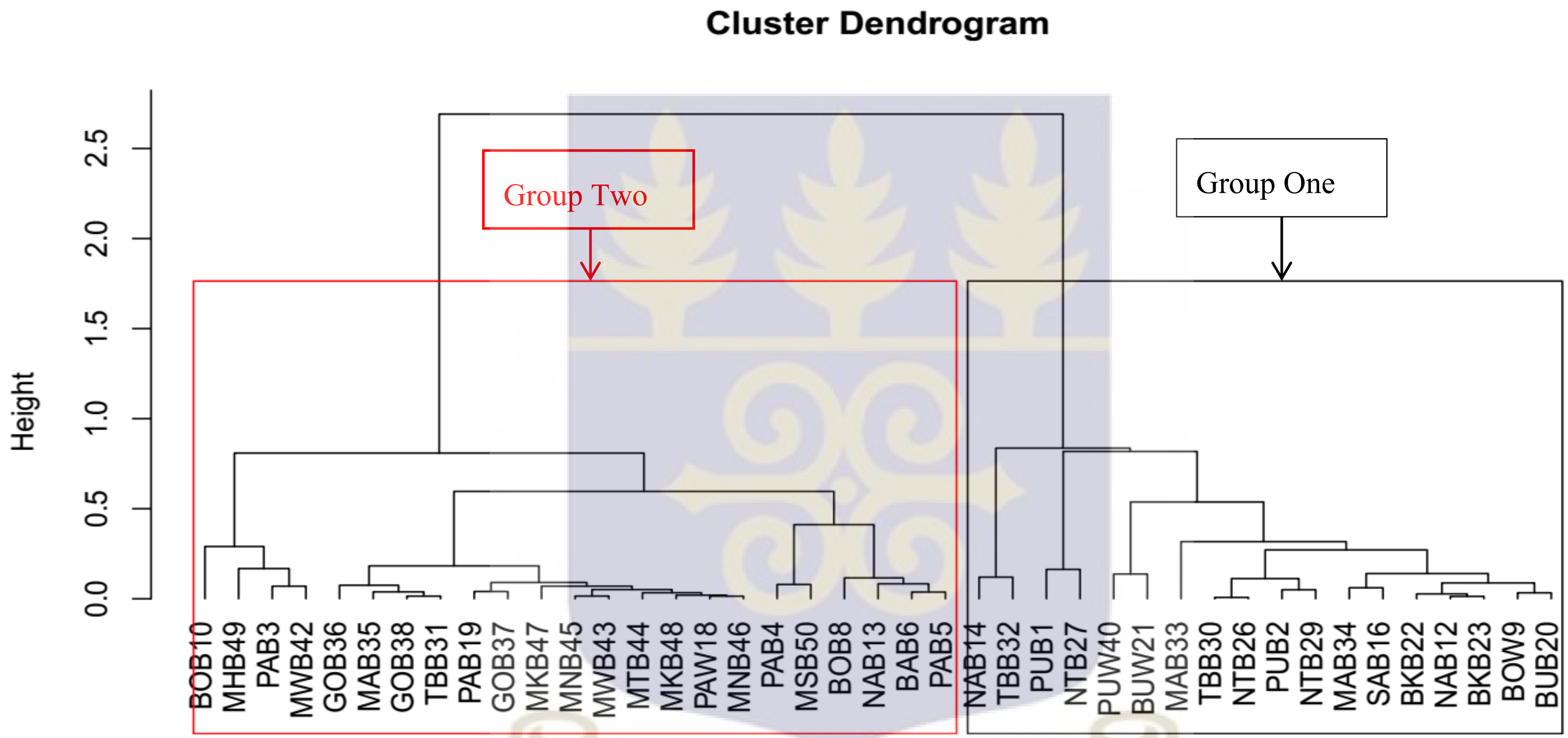

Fig. 4.8: Dendrogram of Hierarchical clustering on first principal component (sorted in order of decreasing scores on component), Black rectangle (Group 1), Red rectangle (Group 2). The water samples are linked into clusters on the x-axis and the linkage distance (height) is plotted on the y-axis.

Based on the clusters defined by the HCA, the groundwater samples in the study area were classified into two major groups. The mean water chemistry of the groups is given in Table 4.5, and the physical significance of the groups defined by the HCA seems to relate to their geographical locations. For instance, to some extent, a significant number of groundwater in group one, were boreholes and hand-dug wells that were mostly sited in the North –East and South-West portions of the catchment where TDS and EC seems to be low (142 to 192 mg/L and 285 to 384 µS/cm for TDS and EC respectively) [Fig. 4.1; Fig. 4.10].

Results of clusters define by the hierarchical cluster analysis (HCA) and individual groundwater scores on principal component (dimensions) 1 and 2 extracted are presented in Fig. 4.9.

Component 1 (Dim 1) explains 35.7% of the total variance and was strongly correlated by TDS, EC, Na^+, Mg^{2+} and Ca^{2+} (Table 4.4). The strong correlation of these hydrochemical parameters to this component (dimension) may suggests some higher degree of water-rock interaction mainly dissolution of minerals in rocks and soil constituents (geology) (Gibrilla et al., 2011).

The groundwater samples classified by HCA as group two (2) obtained positive scores on Component 1 indicating high influence of hydrochemical variables that were correlated to Component 1 (water-rock interactions) . Groundwater sited at BOB10, MWB42, PAB3 and MHB49 recorded higher scores (> 3) on Component 1(Dim1) indicating higher influence of water-rock interactions (Fig. 4.9). However, groundwater samples classified by HCA as group 1 obtained negative scores on Component 1 indicating less influence of water-rock interactions. Groundwater at site BOW9, NAB14, TBB32, PUW40 and

BUB20 recorded a more negative scores on Component 1, this suggest that less mineralisation might have taken place in these groundwater (Fig. 4.10).

Component 2 explains 15.0% of the total variance and was positively correlated by NO_3^- and SO_4^{2-}, and negative correlated by Na^+ and Cl^- (Table 4.4). This indicate that origin of NO_3^- and SO_4^{2-} might be different from that of Na^+ and Cl^-. Groundwater sited at MAB33, MAB34 and SAB16 of group one and NAB13, BOB8, and PAB5 of group two showed more positive scores on component 2 (Fig. 4.9). This indicates significant influence of component 2 factor on that groundwater. Component 2 could be explained to a lesser extent as the contribution of anthropogenic activities like fertilizer application (mainly organic).

Component 3 is moderately correlated by Ca^{2+} and weakly correlated by K^+ and NO_3^-, whereas it was strongly and negatively correlated by temperature (Table 4.4). Component 3 could be explained to a lesser extent as the contribution of activities like fertilizer application (mainly synthetic).

Component 4 which explain 9.67% variance of the data was moderately correlated by K^+ and Cl^- (Table 4.4). Component 5 explained 8.73% variance of the data was strongly correlated by the variable pH (Table 4.4).

Table 4.5: Mean parameter composition and their corresponding standard deviation for the two groups of groundwater in the study area defined by HCA.

	Groups	
Parameters	Group 1 n =18	Group 2 n = 23
T(ºC)	31.67 ±0.9	32.38±1.2
pH	6.84±0.2	6.92±0.2
EC (µS/cm)	334.83±50.1	500.30±87.0
TDS (mg/L)	167.33±25.1	250.22±43.6
Ca^{2+} (mg/L)	31.64±6.7	38.68±9.4
Mg^{2+} (mg/L)	1.52±0.5	3.36±1.1
Na^{+} (mg/L)	50.85±14.3	72.29±29.2
K^{+} (mg/L)	8.18±4.6	9.62±3.2
HCO_3^{-} (mg/L)	213.64±58.3	298.85±82.7
Cl^{-} (mg/L)	17.12±12.9	19.49±11.1
NO_3^{-} (mg/L)	12.89±12.6	14.40±13.5
SO_4^{2-} (mg/L)	5.90±7.9	5.86±5.5

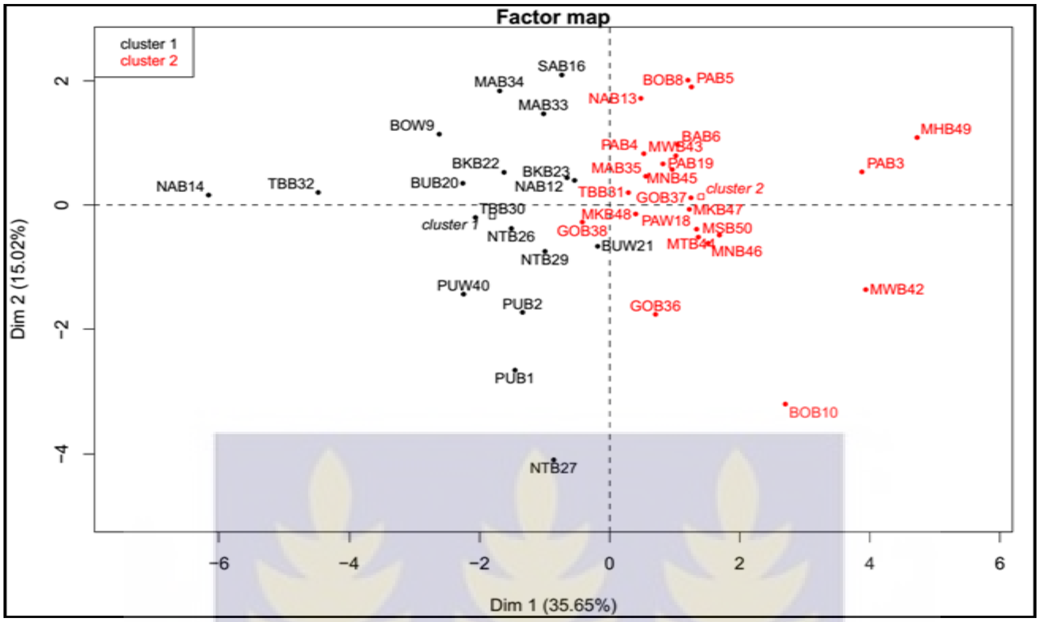

Fig. 4.9: Biplot showing individual groundwater samples scores on Component 1 and 2

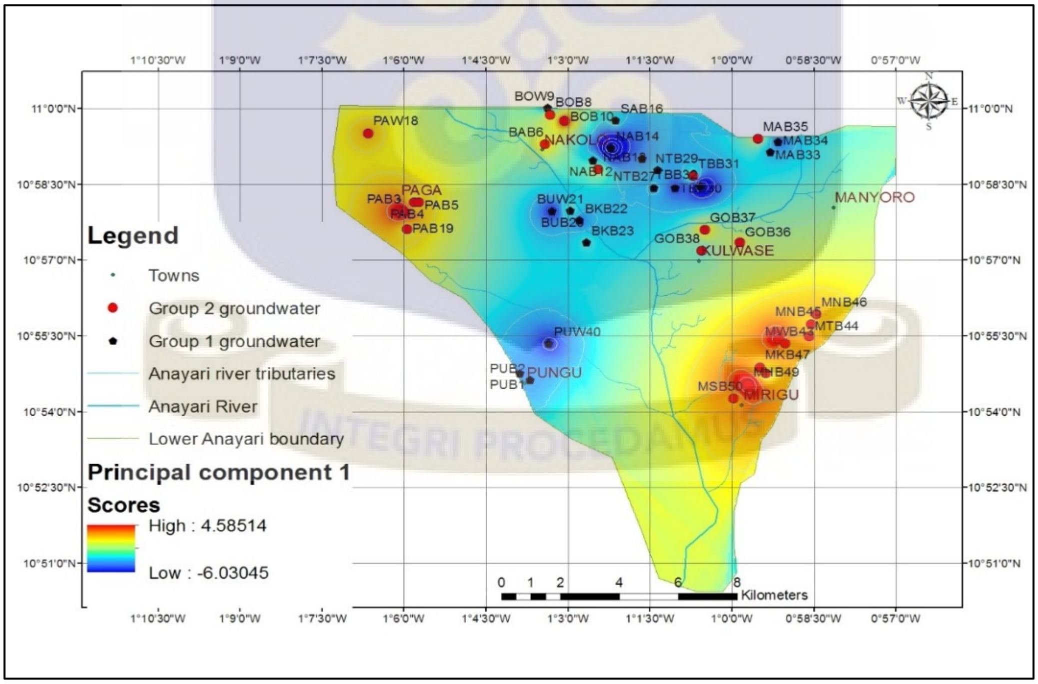

Fig. 4.10: Spatial distribution map showing grouped groundwater samples scores on Component 1 (blue spots indicate possible recharge zone).

4.5 HYDROCHEMICAL FACIES

4.5.1 Piper Diagram

Piper Trilinear plot developed by Piper (1944) was used to study the chemistry and classification of groundwater with respect to key cations and anions such as Na^+, K^+, Ca^{2+} and Mg^{2+}, HCO_3^-, Cl^-, NO_3^- and SO_4^{2-} respectively. The chemical composition of groundwater samples in the Lower Anayari catchment is shown on a Piper diagram (Fig. 4.11).

Three principal hydrochemical water types were identified. These were Ca-Mg-HCO_3, Na-Ca-HCO_3 and Na-HCO_3 water types.

The first water type Ca-Mg-HCO_3 is dominated by alkaline earth metals and weak acids. These water types constitute only about 4% of the groundwater samples in group two.

The second water type Na-Ca-HCO_3 represent waters in which none of the cations and anions exceed 50%; and occupies about 65% of groundwater samples in group two (2) and 83% of groundwater samples in group one (1). The third water type III is Na-HCO_3 this water type constitutes about 17% of groundwater in group one (1) and 39% of groundwater in group two (2). This water type depicts rock-water interaction involving the dissolution of feldspars by the recharging groundwater within the weathered zone above the underlying rocks.

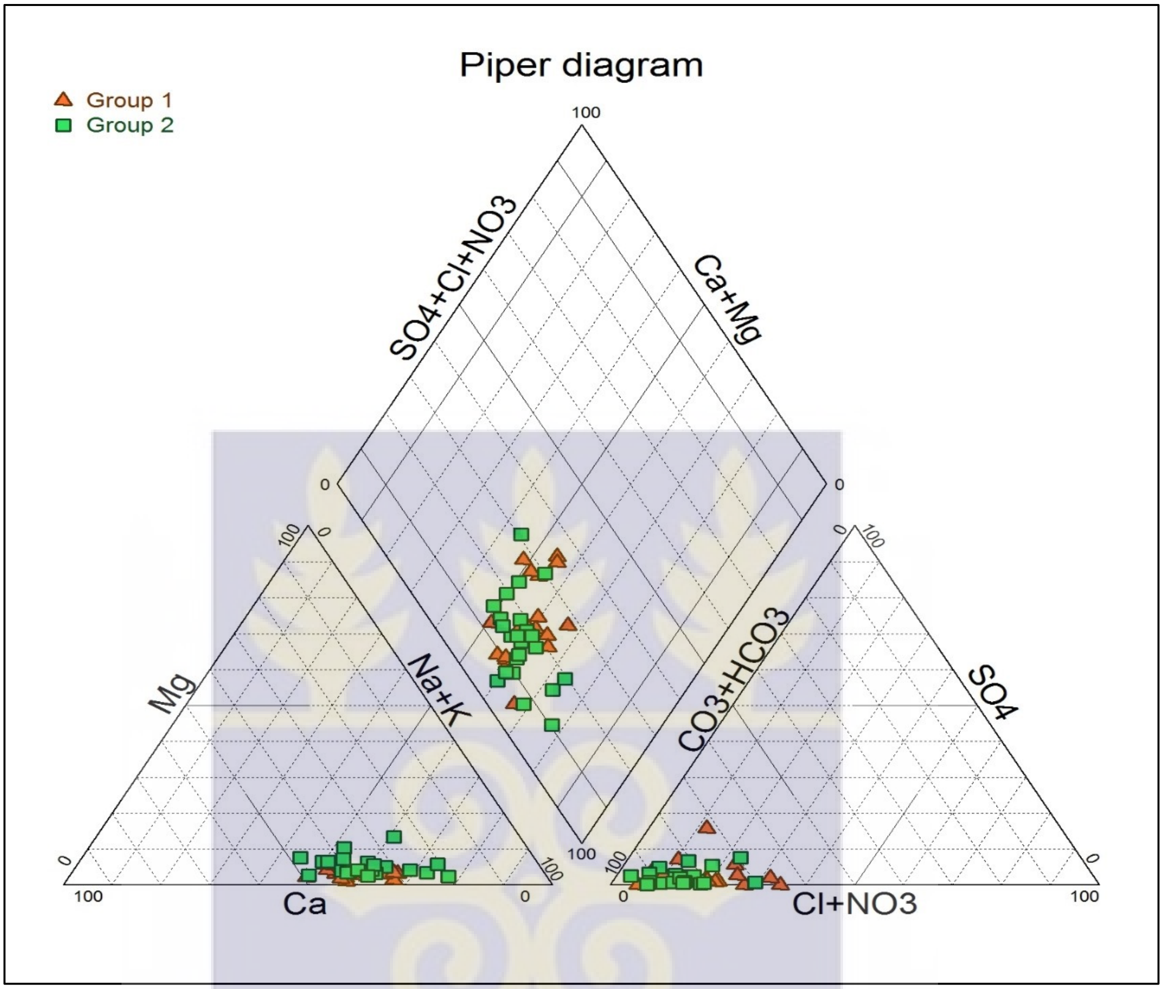

Fig. 4.11: Piper plot of chemical data of groundwater samples in the study area

4.6 TRACE ELEMENT

The levels of trace elements (Fe, Pb, Co, Cd, As and Ni) in all the samples (Table 4.8) were generally low in most of the groundwater samples (mg/L) with concentrations virtually below instrument detection limits. However, levels of trace elements in surface water showed some variability.

4.6.1 Iron (Fe)

The range of iron (Fe) concentration in the water samples ranged from 0.006 to 0.586 mg/L with a mean value of 0.218 mg/L (Table 4.8) for groundwater, varied from 0.006 to 0.120 mg/L with a mean of 0.188 mg/L for irrigation dams, and for Anayari river; it ranged from 0.006 to 0.280 mg/L with a mean of 0.215 mg/L (Table 4.8). However, 65.9% of the groundwater samples and 50 % of Anayari river water samples Fe concentrations were below detection limit of 0.006 mg/L. Averagely the concentration of Fe in water samples were within recommended levels in drinking water (WHO, 2004).

4.6.2 Lead (Pb)

The range of Lead (Pb) concentration in the water samples were from 0.001 to 0.020 mg/L with a mean value of 0.013 mg/L (Table 4.8) for groundwater, varied from 0.001 to 0.002 mg/L for irrigation dams, and for Anayari river; it ranged from 0.001 to 0.008 mg/L with a mean of 0.005 mg/L (Table 4.8). However, 82.9% of the groundwater samples, 75% of irrigation dams and 66.7 % of Anayari river water samples Pb concentrations were below detection limit of 0.001 mg/L. Averagely the concentration of Pb in water samples were above recommended levels in drinking water (WHO, 2004).

4.6.3 Cobalt (Co)

The range of Cobalt (Co) concentration in the water samples were from 0.005 to 0.010 mg/L with a mean value of 0.005 mg/L (Table 4.8) for groundwater, varied from <0.005 to 0.005 mg/L for irrigation dams, and for Anayari river; it ranged from 0.005 to 0.006 mg/L with a mean of 0.005 mg/L (Table 4.8). However, 85.37% of the groundwater samples, 75% of irrigation dams and 50 % of Anayari river water samples Co concentrations were below detection limit of 0.005 mg/L.

4.6.4 Cadmium (Cd)

The range of Cadmium (Cd) concentration in the water samples ranged from 0.002 to 0.006 mg/L with a mean value of 0.004 mg/L (Table 4.8) for groundwater, varied from less than 0.002 to 0.002 mg/L with a mean of 0.002 mg/L for irrigation dams, and for Anayari river; ranged from 0.002 to 0.005 mg/L with a mean of 0.004 mg/L (Table 4.8). However, 85.4% of the groundwater samples, 50% of irrigation dams and 50 % of Anayari river water samples Cd concentrations were below detection limit 0.002 mg/L. Averagely the concentration of Cd in water samples were above recommended levels in drinking water (WHO, 2004).

4.6.5 Arsenic (As)

The range of Arsenic (As) concentration in the water samples were from 0.001 to 0.008 mg/L with a mean value of 0.005 mg/L (Table 4.8) for groundwater, varied from 0.001 to 0.002 mg/L with a mean of 0.002 mg/L for irrigation dams, and for Anayari river; it ranged from 0.001 to 0.006 mg/L with a mean of 0.003 mg/L (Table 4.8). However, 85.4% of the groundwater samples, 50% of irrigation dams and 66.7 % of Anayari river water samples had As concentrations were below detection limit 0.001 mg/L. Averagely the concentration of As in water samples were within recommended levels according the World Health Organization standards (WHO, 2004).

4.6.6 Nickel (Ni)

The range of Nickel (Ni) concentration in the water samples were from 0.001 to 0.019 mg/L with a mean value of 0.001 mg/L (Table 4.8) for groundwater, varied from 0.001 to 0.008 mg/L with a mean of 0.008 mg/L for irrigation dams, and for Anayari river; it ranged from 0.001 to 0.014 mg/L with a mean of 0.013 mg/L (Table 4.8). However, 85.4% of the groundwater samples, 25% of irrigation dams and 50% of Anayari river water samples Ni concentrations were below detection limit 0.001 mg/L. Averagely the concentration of Ni in water samples were within recommended levels (0.02 mg/L) according the World Health Organization standards (WHO, 2004).

4.6.7 Elemental Relationship

A correlations matrix (Table 4.6; Table 4.7) of the trace elements concentrations in the water samples was used to investigate relationships among the trace elements. Generally, the trace elements in the samples demonstrate excellent correlation between elemental pairs; As and Fe, As and Pb, Cd and Fe, and Pb and Fe were strongly correlated in groundwater samples. Also, in groundwater and surface water As was strongly correlated with Cd, Fe and Pb, likewise that of Cd strongly correlated with Fe, Ni and Pb. The strong correlations among the trace elements pairs suggest to less extent that they have a common source. Earlier research in the upper region suggest that the dominant bedrock in the area are the source of the trace elements in the groundwater (Pelig-Ba, 1998). However, findings from trace elements analysis showed the presence of some trace elements in Anayari River. This may have resulted from anthropogenic activities like fertilizer and agro-chemical application.

Table 4.6: Pearson correlation coefficient of trace elements concentrations in ground and surface water at 95% confident interval (bolded)

	As	Cd	Co	Fe	Ni	Pb
As	1					
Cd	**0.72**	1				
Co	0.16	0.25	1			
Fe	**0.96**	**0.74**	0.19	1		
Ni	0.55	**0.69**	-0.28	0.47	1	
Pb	**0.97**	**0.70**	0.30	**0.97**	0.41	1

Table 4.7: Pearson correlation coefficient of trace elements concentrations in groundwater at 95% confident interval (bolded)

	As	Cd	Co	Fe	Ni	Pb
As	1					
Cd	0.75	1				
Co	0.03	0.13	1			
Fe	**0.92**	**0.82**	0.12	1		
Ni	0.48	0.63	-0.51	0.32	1	
Pb	**0.93**	0.75	0.31	**0.96**	0.21	1

Table 4.8: Results of Trace element analysis in mg/L

Sampling Site/Code	Towns	Water Source	Fe	Pb	Co	Cd	As	Ni
PUB1	Pungu	Borehole	**0.021**	<0.001	<0.005	<0.002	<0.001	<0.001
PUB2	Pungu	Borehole	**0.100**	<0.001	<0.005	<0.002	<0.001	<0.001
PAB3	Paga	Borehole	**0.024**	<0.001	<0.005	<0.002	<0.001	<0.001
PAB4	Paga	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
PAB5	Paga	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
BAB6	Banyono	Borehole	**0.035**	<0.001	<0.005	<0.002	<0.001	<0.001
BOB8	Boania	Borehole	**0.165**	**0.006**	**0.005**	**0.002**	**0.003**	**0.012**
BOB10	Boania	Borehole	**0.075**	<0.001	<0.005	<0.002	<0.001	<0.001
NAB12	Nakolo	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
NAB13	Nakolo	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
NAB14	Nakolo	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
SAB16	Nakolo	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
PAB19	Paga	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
BUB20	Buru	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
BKB22	Buru	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
BKB23	Buru	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
NTB26	Navior-Tazika	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
NTB27	Navior-Tazika	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
NTB29	Navior-Tazika	Borehole	**0.015**	<0.001	<0.005	<0.002	<0.001	<0.001
TBB30	Tazika-Batua	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
TBB31	Tazika-Batua	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
TBB32	Tazika-Batua	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
MAB33	Manyoro	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
MAB34	Manyoro	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
MAB35	Manyoro	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001

GOB36	Gomowo	Borehole	**0.061**	<0.001	<0.005	<0.002	<0.001	<0.001
GOB37	Gomowo	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
GOB38	Gomowo	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
MWB42	Mirigu	Borehole	**0.433**	**0.015**	**0.006**	**0.003**	**0.005**	**0.008**
MWB43	Mirigu	Borehole	**0.515**	**0.018**	**0.010**	**0.005**	**0.006**	**0.010**
MTB44	Mirigu	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
MNB45	Mirigu	Borehole	**0.485**	**0.014**	**0.003**	**0.005**	**0.005**	**0.015**
MNB46	Mirigu	Borehole	**0.586**	**0.020**	**0.005**	**0.006**	**0.008**	**0.019**
MKB47	Mirigu	Borehole	**0.518**	**0.017**	**0.004**	**0.004**	**0.007**	**0.011**
MKB48	Mirigu	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
MHB49	Mirigu	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
MSB50	Mirigu	Borehole	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
BOW9	Boania	Hand-dug well	**0.026**	<0.001	<0.005	<0.002	<0.001	<0.001
PAW18	Paga	Hand-dug well	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
BUW21	Buru	Hand-dug well	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
PUW40	Pungu	Hand-dug well	<0.006	**0.004**	<0.005	<0.002	<0.001	<0.001
NAD15	Nakolo	Irrigation dam	**0.188**	**0.002**	**0.005**	**0.002**	**0.002**	**0.008**
BOS17	Boania	Irrigation dam	**0.152**	<0.001	<0.005	<0.002	**0.002**	**0.006**
BKS24	Buru	Irrigation dam	**0.071**	<0.001	<0.005	<0.002	<0.001	<0.001
NTS28	Navior-Tazika	Irrigation dam	**0.083**	<0.001	<0.005	**0.002**	<0.001	**0.008**
BAS7	Banyono	River	**0.160**	**0.005**	**0.005**	**0.003**	**0.002**	**0.008**
BOS11	Boania	River	**0.280**	**0.008**	**0.006**	**0.005**	**0.004**	**0.014**
BKS25	Buru	River	**0.204**	**0.003**	**0.005**	**0.003**	**0.002**	**0.013**
PUS39	Pungu	River	<0.006	**0.003**	<0.005	<0.002	<0.001	<0.001
DOS41	Doba	River	<0.006	<0.001	<0.005	<0.002	<0.001	<0.001
MIS51	Mirigu	River	<0.006	<0.001	<0.005	<0.002	**0.006**	<0.001

4.7 WATER QUALITY

Hydrochemical data in this study have been evaluated in terms of its suitability for drinking and irrigation purposes. The analytical results were compared with the standard guideline values recommended by the World Health Organisation (WHO, 2004).

4.7.1 Water Quality Index

The water quality index (WQI) proposed by Tiwari and Mishra, (1985) was used to assess the suitability of the water in the study area for drinking. This was calculated using equations below;

$$\mathrm{WQI} = \mathrm{Anti\ log}\left(\textstyle\sum_{n=1}^{n} \mathrm{W_n} \log_{10} \mathrm{q_n}\right) \tag{4.10}$$

where,

W_n is the weighting factor, calculated from equation (4.6)

$$\mathrm{W_n} = \mathrm{K}(\mathrm{S_i})^{-1} \tag{4.11}$$

with K the proportionality constant derived from equation (4.7)

$$\mathrm{K} = \left[\textstyle\sum_{n=1}^{n} (\mathrm{S_i})^{-1}\right]^{-1} \tag{4.12}$$

the S_i are the standard values of the water quality parameter (WHO, 2004).

Quality rating (q_n) was calculated using equation (4.8)

$$\mathrm{q_n} = \left[\frac{(\mathrm{V_{actual}} - \mathrm{V_{ideal}})}{(\mathrm{V_{standard}} - \mathrm{V_{ideal}}}\right] \times 100 \tag{4.13}$$

where,

q_n Quality rating of $i\,th$ parameter for a total of n water quality parameters; V_{actual} is the value of the water quality parameter obtained from laboratory analysis;

V_{ideal} is the value of that water quality parameter which was obtained from the standard tables, V_{ideal} for pH = 7, and all other parameters was equivalent to zero; $V_{standard}$ is the standard of the water quality parameter (WHO, 2004). The parameters used in assessing the water quality are presented in Table 4.9

Table 4.9: Water quality parameters, their standard values, their ideal values and the assigned weighting factors

Parameter	WHO Standard Value, S_i	Ideal Value, V_{ideal}	$(S_i)^{-1}$
pH	8.5	7	0.11765
EC (µS/cm)	1200	0	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
Pb (mg/L)	0.01	0	100
Cd (mg/L)	0.003	0	333.333
As (mg/L)	0.01	0	100
Ni (mg/L)	0.02	0	50

The calculated WQI values are then used to rate the groundwater quality as excellent, good, poor, very poor and unfit for human consumption (Table 4.10).

Table 4.10: Water Quality Index Scale

Water Quality	Description
0 - 25	Excellent
26 - 50	Good
51 - 75	Poor
76 - 100	Very Poor
> 100	Unfit for Drinking (UFD)

The results of the computed WQI values of group one boreholes ranged from 0.230 to 87.73, while that of group two ground waters and the surface waters range from 0.470 to 159.9 and 9.630 to 2134, respectively. The groundwater and surface water in the catchment exhibited some degree of water quality variability, a summary of water quality of groundwater and surface water is presented below (Table 4.11).

Table 4.11: Summary of water quality result of groundwater (Group 1 and Group 2) and surface water

Water Samples	Water Quality Index Category (%)				
	Excellent	Good	Poor	Very poor	Unfit for drinking
Group 1	61.1	16.7	16.7	5.6	-
Group 2	56.5	8.7	8.7	8.7	17.4
Surface	30	20	30	-	20

Fig. 4.12 shows the spatial distribution of the WQI in the study area. From the figure, groundwater in Nakolo and Mirigu towns showed “poor” to “unfit for drinking” water quality. Similarly, groundwater in these towns showed higher nitrate levels (Fig. 4.13) which are associated with fertilizer and agrochemical application farm practices.

Hence, though the water quality might be affected by the geological material which seems to contribute to the presence of some trace elements which are of great concern, leaching from point source pollutants from agricultural wastes (agrochemicals, fertilizers, etc.) seems to be probable factors also affecting water quality in the area. Also, the surface water seems to be polluted by anthropogenic activities.

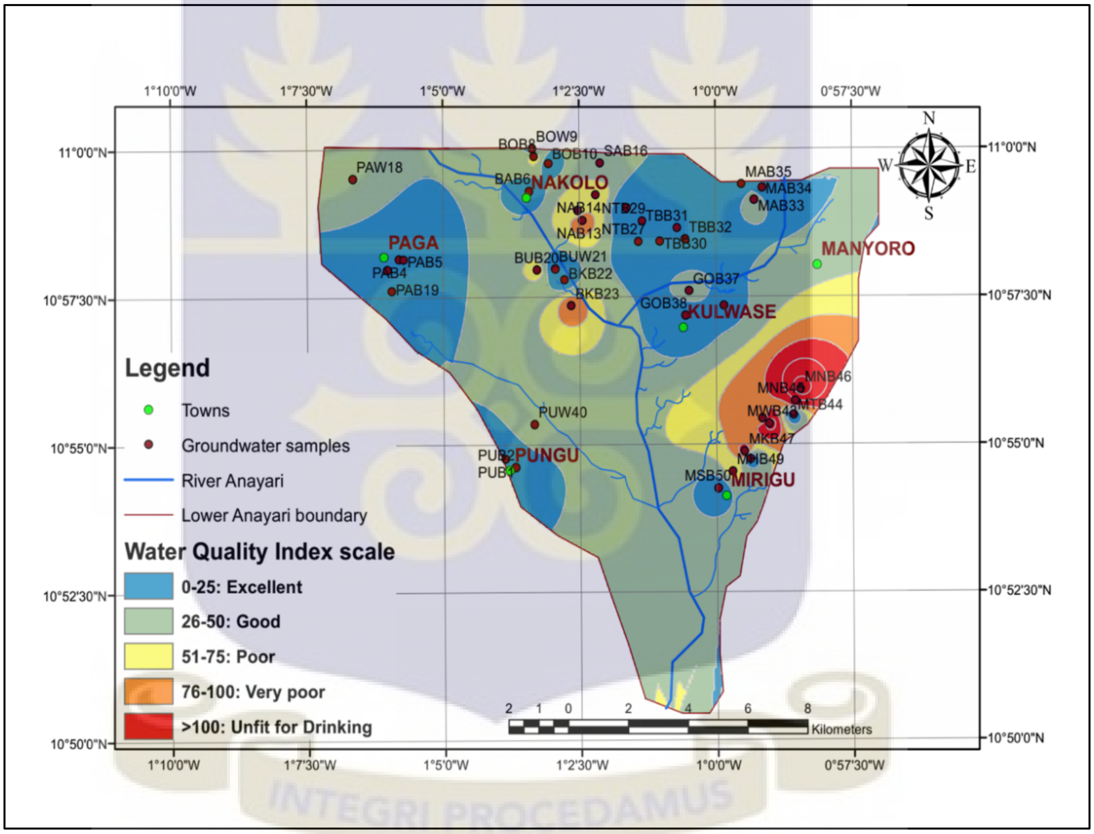

Fig. 4.12: WQI distribution map of the study area

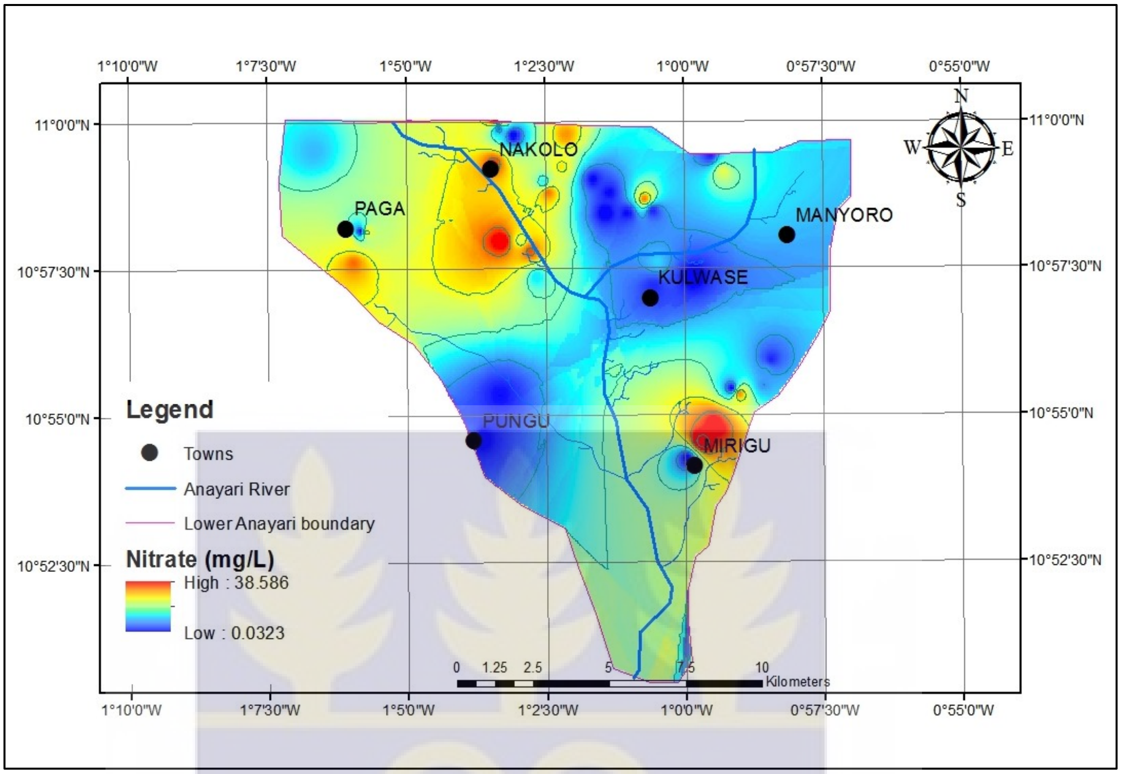

Fig. 4.13: Spatial distribution of Nitrate levels in the study area

4.7.2 Water quality for Irrigation Purpose

The sodium adsorption ratio (SAR), sodium percentage (%Na), and residual sodium carbonate (RSC) are the important parameters that can be used to access the suitably of water for irrigation purposes. However, combination of electrical conductivity (EC) and sodium concentration are very important parameters in the classification of the irrigation water (Tiwari and Singh, 2014).

In this study the mentioned parameters were used to access the suitability of groundwater and surface water for irrigation.

4.7.2.1 Sodium Adsorption Ratio (SAR)

High sodium concentration leads to development of undesirable soil properties (formation of crust, water-logging, reduced soil aeration, reduced infiltration rate and reduced soil permeability) (Kelly, 1951). Therefore, in assessing the suitability of groundwater for irrigation, Na^+ concentration is essential. SAR characterises the degree to which irrigation water enters into cation exchange reactions in soil (Manjusree et al., 2009). SAR is defined as;

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}} \tag{4.14}$$

Sodium adsorption ratio (SAR) are classified into four categories as S1 (SAR<10), S2 (10-18), S3 (18-26) and S4 (>26) and defined as low, medium, high and very high respectively. The total concentration of soluble salts in term of electrical conductivity in irrigation water can be expressed as low (EC <250 µS/cm), medium (250- 750 µS/cm), high (750-2250 µS/ cm) and very high (>2250 µS/cm) and defined as C1, C2, C3 and C4 salinity zone respectively (USSL, 1954).

The sodium adsorption ratio (SAR) of groundwater was plotted on the USSL , (1954) diagram with the exception of surface water because of their EC values were < 100 µS/cm. From the plot it was evident that most of the groundwater samples fall in the category of C2S1 and a few on C1S1 denoting excellent to good quality of water for irrigation (Fig. 4.14).

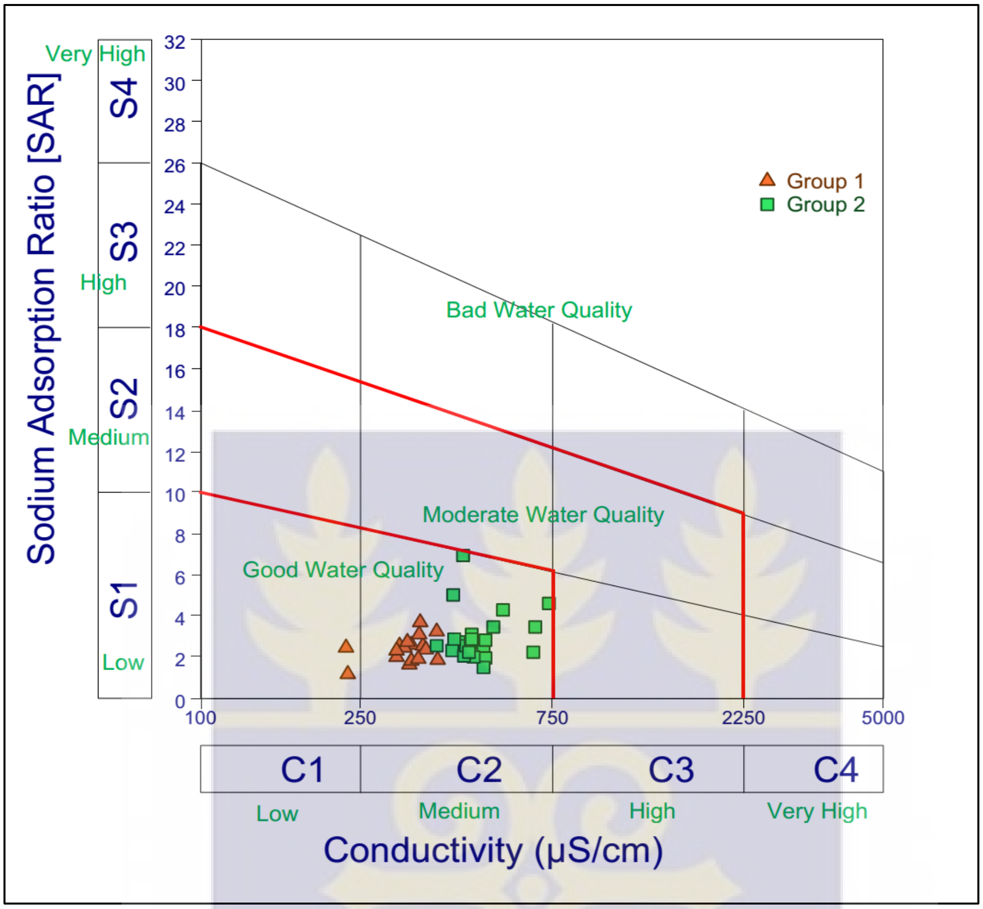

Fig. 4.14: US salinity diagram (USSL) for classification of irrigation water

4.7.2.2 Sodium Percentage (%Na)

Na^+ concentration expressed as sodium percentage in water is widely use in assessing the suitability of water for irrigation purposes (Wilcox, 1955).

It is usually calculated by the following relation:

$$\%Na = \left(\frac{Na^{+}+K^{+}}{Ca^{2+}+Mg^{2+}+K^{+}+Na^{+}}\right) \times 100 \qquad (4.15)$$

The calculated Na% (meq/l) of the samples was plotted against electrical conductivity in µS/cm (Fig. 4.15).

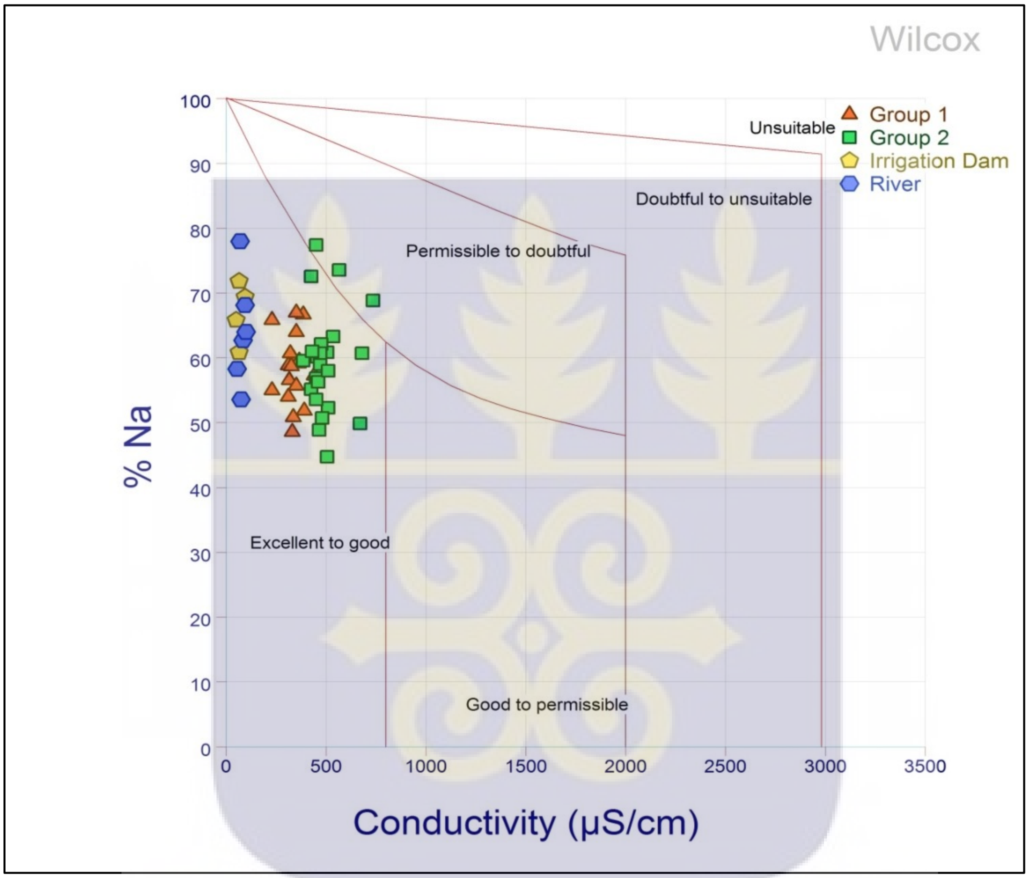

Fig. 4.15: Rating of groundwater samples on the basis of electrical conductivity and percentage sodium [after (Wilcox, 1955)].

The results revealed that 100% of the surface water, 100% of the groundwater in group 1 and 87.0 % of groundwater in group two fell in the field of excellent to good while 13.4% of the group two groundwater samples (BOB10, MSB50, MHB49) fell under permissible to doubtful.

4.7.2.3 Residual Sodium Carbonate

The difference between the excess sum of carbonate and bicarbonate in groundwater against the sum of calcium and magnesium and is denoted by 'residual sodium carbonate' (RSC). In addition to the SAR and Na%, it also has a significant effect on groundwater suitability for irrigation. The High excess carbonate concentration often known as "residual" combines with calcium and magnesium to form a solid scale-like material which settles out of the water and this is known to deteriorate water quality (Sundaray et al., 2009). This excess is determined by the equation below (Richard, 1954).

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \tag{4.16}$$

RSC <1.25 meq/L is safe for irrigation, values between 1.25 to 2.5meq/L are of marginal quality and a value >2.5 meq/L is unsuitable for irrigation (Nagaraju et al., 2006). In this study, the surface water, the group 1 groundwater and group 2 groundwater show RSC values ranging from 0.16 to 1.51 meq/L, 0.56 to 3.76 meq/L and from 0.81 to 6.17 meq/L respectively. The results showed some degree of variability of water quality for irrigation according to this index. The result of residual sodium carbonate (RSC) calculations of samples in the study area is presented below (Table 4.12).

Table 4.12: Suitability of water in the study area for irrigation based on RSC

Percentage (%) of samples			RSC	Remarks on quality
Group 1	Group 2	Surface water		
27.8	4.35	90	< 1.25	Safe
55.6	52.2	10	1.25 – 2.5	Marginal quality
16.7	43.5		> 2.5	Unsuitable

4.8 STABLE ISOTOPE

The composition of oxygen-18 and deuterium of the surface water (irrigation dams, and Anayari River) and groundwater (hand-dug wells and borehole) are presented in (Table 4.1 and Table 4.2 respectively).

Results of isotopic composition of the sources of water in the study area were plotted on δ^{18}O vrs δD diagram, as shown in (Fig. 4.16).

Two meteoric water lines were inserted, these are the Global Meteoric Water Line (GMWL) (Coplen, 1996) and Local Meteoric Water Line equation (LMWL) (Akiti, 1980). The Global Meteoric Water Line (GMWL) is given as;

$$\delta^{2}H‰/_{VSMOW} = 8\delta^{18}O‰/_{VSMOW} + 10 \qquad (4.17)$$

Local Meteoric Water Line (Akiti, 1980) is given as;

$$\delta^{2}H‰/_{VSMOW} = 7.86\delta^{18}O‰/_{VSMOW} + 13.61 \qquad (4.18)$$

The work by Akiti (1980) was in the Accra plains in the South-Eastern part and Upper Regions of Ghana. The study area, lies in the Upper region of Ghana, hence, LMWL (Akiti, 1980) was the adequate parameter for the studies.

4.8.1 Isotope composition of Anayari River

The δD and δ^{18}O isotopic composition of the Anayari River ranges from -10.53 to -18.70‰/VSMOW and -2.66 to -3.73‰/VSMOW, with a mean isotopic composition of -15.89‰/VSMOW and -3.25‰/VSMOW for δD and δ^{18}O, respectively. The depleted

$\delta^{18}O$ isotopic signature was measured at the lower course of the river (DOS41), while the enriched $\delta^{18}O$ isotopic signature was measured at PUS39 a tributary of the river. The River Anayari represents an ephemeral river, this is evident by the relatively less enriched isotopic composition. This largely represents the signature of precipitation during the sampling event. All of the sampling points were below the LMWL indicating evaporation effect. However, isotopic data of the river plotted were along the GMWL indicating their origin is meteoric.

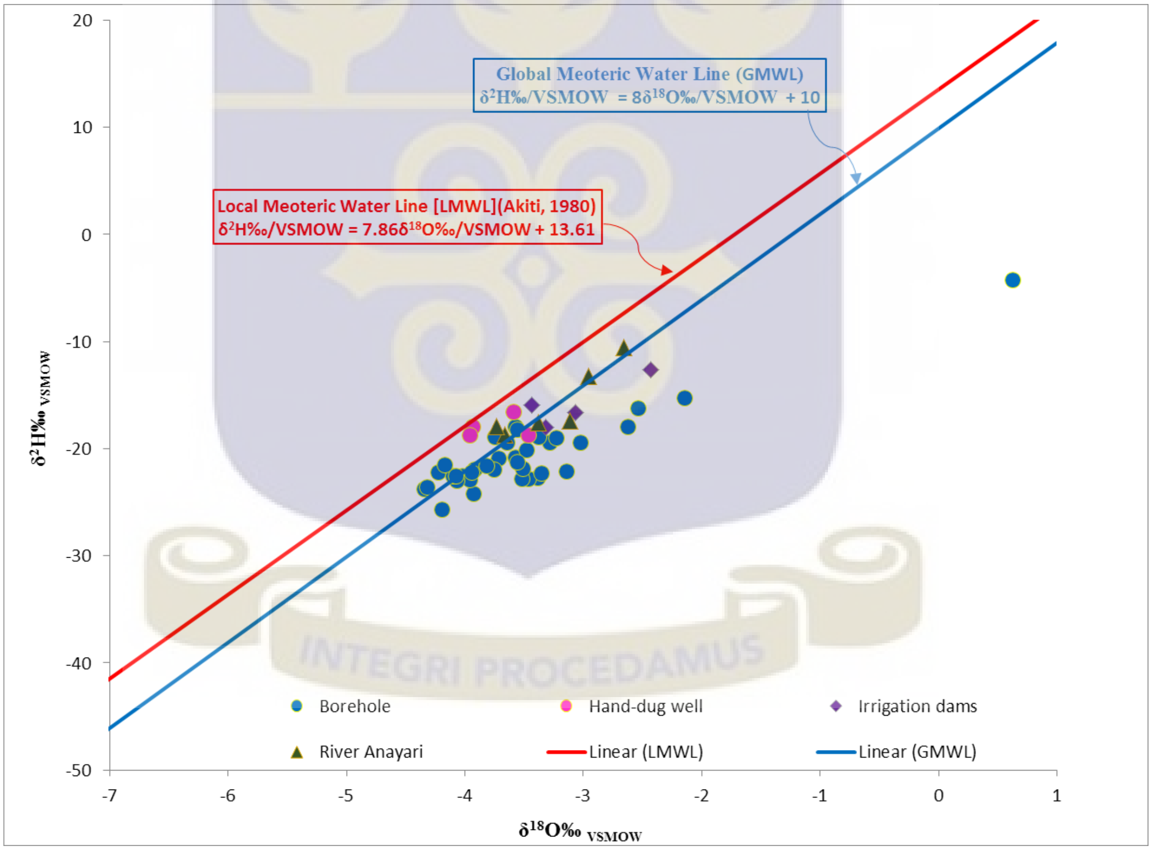

Fig. 4.16: A plot $\delta^{18}O - \delta^{2}H$ showing relationships for isotopic composition of Akiti (1980) (LMWL), GMWL, surface water (irrigation dams and Anayari River) and groundwater (boreholes and hand-dug wells).

4.8.2 Isotope composition of irrigation dams

The isotopic content of irrigation dams in the study area ranges from -2.43 to -3.44‰/VSMOW and –12.6 to -18‰/VSMOW for δ^{18}Oand δD respectively, with a mean isotopic composition of -3.06‰/VSMOW and -15.79‰/VSMOW for δ^{18}O and δD respectively. They were plotted below the LMWL and GMWL due to their open nature and general exposure to atmospheric conditions; they are much more prone to evaporative enrichment arising from high ambient temperatures and low relative humidities prevailing in the areas. The isotope composition data of irrigation dams were along an evaporation line (Fig. 4.18) defined by the equation below with $R^2 = 0.712$;

$$\delta^2H‰/_{VSMOW} = 5.16268^{18}O‰/_{VSMOW} + 0.07 \qquad (4.19)$$

4.8.3 Isotope composition of groundwater (Boreholes and Hand-dug wells)

The isotopic content of groundwater (boreholes) in the study area ranges from 0.62 to -4.35‰/VSMOW and from -4.2‰ to -25.65‰/VSMOW for δ^{18}O and δD respectively, with a mean isotopic composition of –3.51‰/VSMOW and -20.64‰/VSMOW. Similar mean isotopic composition were obtained in Paga and Bolgatanga in the Upper east region of Ghana by Akiti (1980, 1982). The high enriched isotopic composition of value 0.62‰/VSMOW and -4.2‰/VSMOW δ^{18}O and δD respectively was observed in groundwater sited at BKB23, and this indicates that it has been recharged by an enriched source or might have experience a significant evaporation before recharge.

The isotopic content of hand-dug wells on the other hand, ranged from -3.47 to -3.96 ‰/VSMOW and -16.55 to -18.70‰/VSMOW for δ^{18}O and δD respectively, with a mean

$\delta^{18}O$ and $\delta^{2}H$ content of -3.74‰/VSMOW and -17.96‰/VSMOW respectively. They were plotted along the LMWL indicating probable direct percolation with less evaporation; this seems possible if hand-dug wells are partially covered.

The groundwater (borehole) data fell on and along an evaporation line (Fig. 4.17) defined by the equation;

$$\delta^{2}H‰/_{VSMOW} = 3.8351\delta^{18}O‰/_{VSMOW} - 7.1925 \qquad (4.20)$$

The evaporation line has a lower slope and deuterium excess than the GMWL, and is thus indicative of the effects of high evaporation rates, high temperatures, low relative humidity, and slow infiltration rates through the unsaturated zone.

However, the nature and thickness of the overburden material and the prevailing weather conditions governs the fraction of precipitation that reaches the saturated zone as direct groundwater recharge from precipitation (Yidana, 2013).

The slope of the Borehole water evaporation Line (BWL) was comparatively lower than those observed for the LMWL (Fig. 4.17). This suggests that evaporation of raindrops before recharge was evident or infiltrating rainwater underwent some evaporation prior to recharge. In (Fig. 4.17), the LMWL and BWL lines intersect at a point where $\delta^{2}H$ and $\delta^{18}O$ are respectively -26‰/VSMOW and -5‰/VSMOW. This is the signature of the rainwater that recharged the groundwater and other surface water in the study area (Akiti, 1980).

4.8.4 Interaction between surface flows and groundwater in the catchment

The understanding of any possible relationship between surface flows in river and irrigation dams/ponds, and the aquifers in the catchment, forms an important aspect of characterizing the hydrological system (Yidana, 2013). The river and irrigation dams/ponds generally present enriched water compared to groundwater (borehole). This suggests that most hydraulic connection between surface flows and the aquifers in the catchment favours groundwater discharge into the surface water bodies. On the contrary, groundwater sited in Buru (BKB23) seems to be recharged by an enriched source.

An attempt has been made to determine the isotopic signature of groundwater (borehole) source and surface flow in the area for possible hydraulic connectivity. This was determined through a simultaneous solution of the River evaporation line (RWL) and Borehole evaporation line (BWL) (Fig. 4.17), and also between Irrigation dams evaporation line (IDWL) and Borehole evaporation line (BWL) (Fig. 4.18) (Yidana, 2013).

The simultaneous solution of RWL and BWL resulted in -4.44‰/VSMOW and -24.22‰/VSMOW for $\delta^{18}O$ and $\delta^{2}H$ respectively (Fig. 4.17). This is certainly within the range of isotope signature of meteoric water recharging ground and surface waters in the catchment. Likewise, these values are within the range of the isotope data of groundwater observed in the catchment. The implication is that groundwater may contribute to local river flow in the catchment.

Also in (Fig. 4.18), the IDWL intersects the BWL at point -5.46‰/VSMOW and -28.13‰/VSMOW for $\delta^{18}O$ and $\delta^{2}H$ are respectively. Similarly, this is certainly within the range of isotope signature of meteoric water recharging ground and surface waters in the catchment, but outside range of isotope data for the groundwater in the catchment as captured in this study.

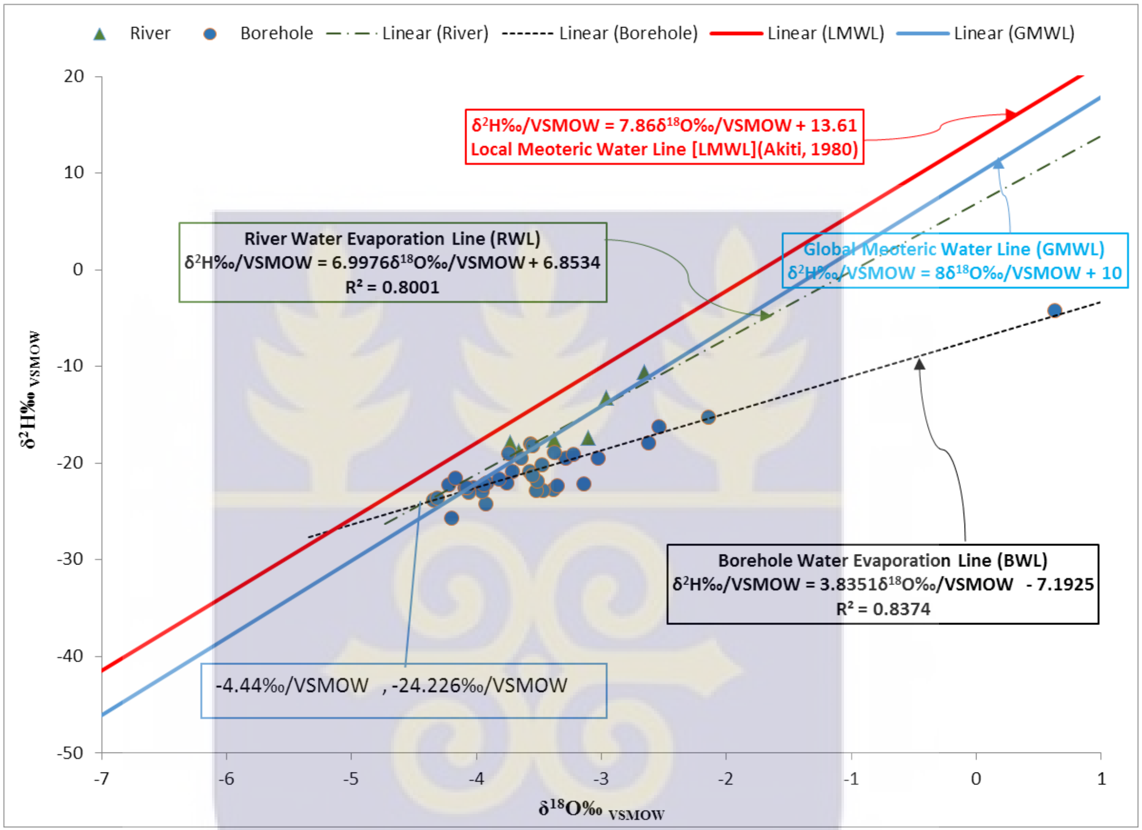

Fig. 4.17: Relationship between the RWL and BWL in the study area

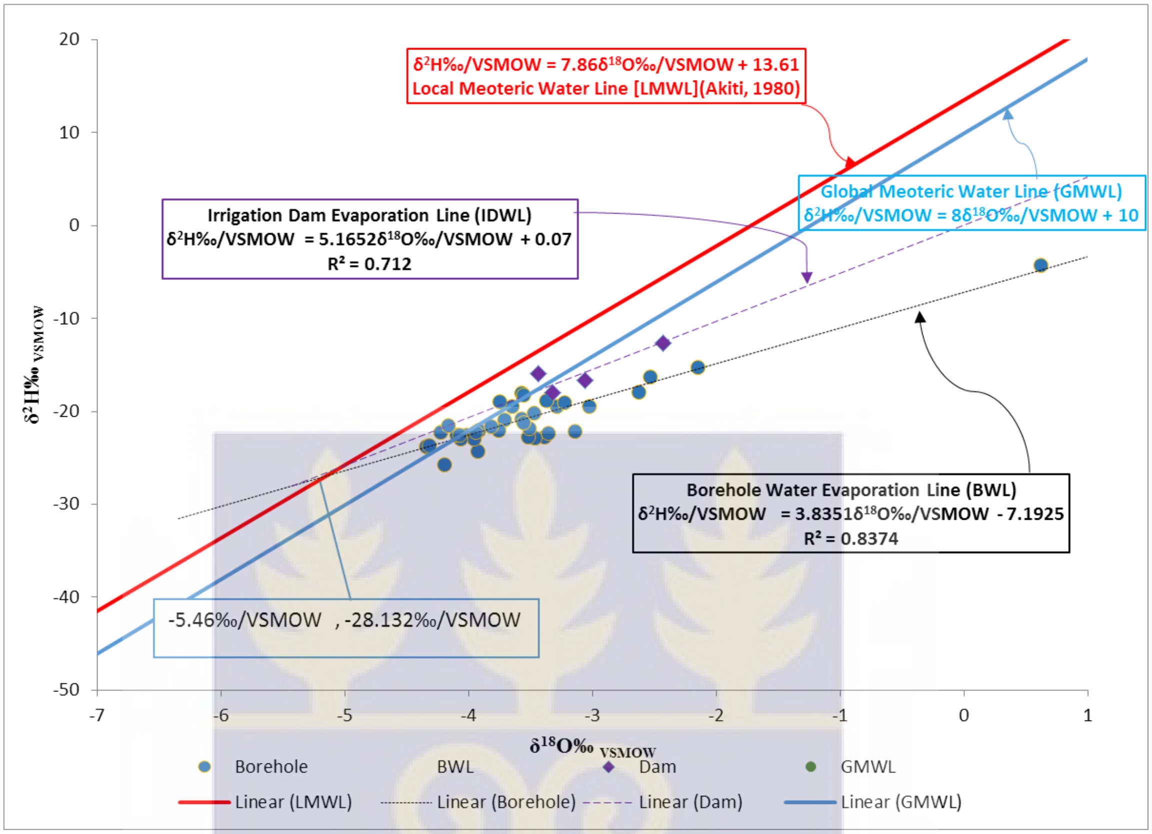

Fig. 4.18: Relationship between the IDWL and BWL in the study area

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

This chapter outlines the main conclusions of the research carried out with the main objectives of the using geochemical and isotopic techniques to assess the quality of groundwater in the Lower Anayari Catchment of the Upper East Region of Ghana, due to intensive farming activities by the people within the catchment.

The analysis of the main chemical parameters, using R-statistics, bivariate plots of major cations and anions, Piper diagram and geostatistics were applied to the hydrochemical data set to provide insight into spatial, geochemical processes and pollution as well as water quality in the study area. The analysis of the hydrochemical data from the Lower Anayari catchment area has revealed the groundwater pH to be generally near neutral and near alkaline. The general trend of major cations and anions, and trace element concentration were $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$, $HCO_3^- > Cl^- > NO_3^- > SO_4^{2-}$, and Fe > Pb > As > Co > Cd > Ni respectively.

The hydrochemical facies were Ca-Mg-HCO_3, Na-Ca-HCO_3 and Na-HCO_3. These facies are formed dominantly by weathering–dissolution mechanism, mostly incongruent dissolution of silicate minerals, cation exchange reaction. The Hierarchical Cluster Analysis (HCA) further classified the groundwaters of the study area into two groups. The advantage of the method was that the groups were objective, and clear geo-hydrological patterns were recognized. The groups show different degrees of water-rock interaction or mineralisation. Group one groundwater samples were characterised as a less mineralised with 77.8% of them being “excellent to good water” whilst 22.2% of such water were found to be “poor to very poor”. Group two (2) groundwater were characterised by highly mineralised groundwater with 65.2% of them being “excellent to good” whilst 34.8% of such water were found to be, “poor to unfit for drinking” water quality.

The suitability of water from the study area for irrigation was assessed by using the USSL salinity, Wilcox diagram and residual sodium carbonate (RSC). The USSL salinity and Wilcox diagram methods revealed that the groundwaters from the study area are good for irrigation. However, suitability of water in the study area for irrigation based on RSC indicates that 83.3% and 56.5% of group one and two respectively are of “safe to marginal quality” for irrigation.

The stable isotopes composition measurements for groundwater, River Anayari and irrigation dams, clustered closely along the global meteoric water line (GMWL) suggesting an integrative recharge from meteoric origin. However, few groundwater samples, clustered below the global meteoric water line (GMWL) showing they were fractionated before recharge. Similarly, isotopic composition of some of the River Anayari and irrigation dams samples were plotted below the GMWL suggesting they are enriched arising from high ambient temperatures and low relative humidities prevailing in the study area.

Lastly, isotopic data suggest possible interactions of surface flow and groundwater flow in Lower Anayari Catchment.

5.2 RECOMMENDATIONS

The human population living in the Lower Anayari catchment area depend on groundwater to improve upon their socio-economic livelihood; therefore, the following are recommended:

i) A comprehensive geochemical study in Upper Anayari catchment should be encouraged to help define the recharge and discharge zones in the entire catchment, so as to protect the recharge zones from anthropogenic activities. Estimation of the recharge rate will also be very important since the catchment depends on groundwater for their day-to-day activities.

ii) Although the study showed that groundwater in Paga, Kulwase, and Pungu were of excellent chemical quality, it is recommend that good agricultural practices and good sanitation should be encouraged in order to protect the groundwater from pollution.

iii) Groundwater in and around Manyoro, Nakolo, and Mirugu communities should be monitored on a monthly basis since they showed deteriorating water quality.

iv) Finally a policy be enacted to protect the surface waters in LAC since there exit some hydraulic connection between surface flow and groundwater.

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APPENDIXES

Appendix A. 1: Percentage charge balance error

Sampling ID	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	Total Cations ($Na^+ + K^+ + Ca^{2+} + Mg^{2+}$)	Total Anions ($HCO_3^- + Cl^- + SO_4^{2-}$)	%CBE
PUB1	2.829	0.197	1.357	0.151	3.359	1.198	0.000	4.533	4.558	**-0.270**
PUB2	2.607	0.128	1.996	0.106	4.239	0.339	0.084	4.837	4.663	**1.831**
PAB3	2.907	0.463	2.954	0.439	5.759	0.559	0.483	6.763	6.801	**-0.280**
PAB4	2.019	0.240	0.958	0.491	3.279	0.284	0.181	3.709	3.745	**-0.480**
PAB5	2.002	0.233	1.597	0.444	3.999	0.164	0.134	4.275	4.297	**-0.259**
BAB6	2.646	0.233	1.996	0.193	4.719	0.197	0.111	5.068	5.027	**0.404**
BOB8	2.637	0.179	1.597	0.266	4.639	0.082	0.126	4.679	4.848	**-1.771**
BOB10	7.311	0.309	1.996	0.230	8.399	0.929	0.044	9.847	9.371	**2.474**
NAB12	2.502	0.228	1.597	0.227	4.319	0.177	0.081	4.554	4.578	**-0.260**
NAB13	1.614	0.189	1.916	0.312	3.040	0.558	0.334	4.032	3.931	**1.272**
NAB14	0.814	0.353	0.878	0.078	1.520	0.455	0.001	2.123	1.976	**3.591**
SAB16	1.845	0.217	1.757	0.160	3.119	0.095	0.676	3.980	3.890	**1.134**
PAB19	2.198	0.223	2.036	0.311	3.999	0.496	0.283	4.767	4.779	**-0.121**
BUB20	1.606	0.207	1.836	0.081	2.960	0.459	0.112	3.731	3.531	**2.754**
BKB22	2.193	0.238	1.437	0.138	3.519	0.361	0.064	4.007	3.944	**0.787**
BKB23	2.463	0.253	1.757	0.119	4.479	0.161	0.181	4.592	4.821	**-2.434**
NTB26	2.111	0.199	1.437	0.131	3.119	0.851	0.046	3.878	4.016	**-1.746**
NTB27	3.573	0.153	1.757	0.081	5.599	0.332	0.000	5.564	5.931	**-3.194**
NTB29	2.833	0.128	1.517	0.148	3.839	1.017	0.045	4.626	4.902	**-2.893**
TBB30	2.067	0.179	1.437	0.129	3.279	0.671	0.077	3.812	4.027	**-2.742**
TBB31	2.528	0.312	2.116	0.199	3.599	1.070	0.041	5.155	4.710	**4.510**
TBB32	1.736	0.156	0.878	0.101	2.400	0.550	0.040	2.872	2.989	**-1.999**

MAB33	2.694	0.033	1.757	0.163	4.479	0.155	0.046	4.646	4.680	**-0.362**
MAB34	1.697	0.072	1.517	0.194	3.279	0.151	0.099	3.480	3.530	**-0.717**
MAB35	2.080	0.269	1.717	0.314	3.999	0.594	0.034	4.379	4.627	**-2.756**
GOB36	2.733	0.233	2.116	0.181	4.439	0.938	0.072	5.262	5.450	**-1.750**
GOB37	3.177	0.279	1.916	0.184	5.439	0.232	0.194	5.555	5.865	**-2.709**
GOB38	2.463	0.230	1.637	0.194	3.919	0.595	0.098	4.524	4.612	**-0.962**
MWB42	4.234	0.335	2.635	0.316	6.719	0.960	0.067	7.520	7.745	**-1.477**
MWB43	2.724	0.207	1.717	0.314	4.399	0.433	0.135	4.962	4.968	**-0.053**
MTB44	5.044	0.263	1.757	0.248	6.079	0.842	0.147	7.311	7.067	**1.696**
MNB45	2.868	0.148	1.677	0.280	4.559	0.256	0.044	4.973	4.860	**1.149**
MNB46	3.129	0.174	2.156	0.242	4.719	0.792	0.051	5.700	5.562	**1.226**
MKB47	2.776	0.120	2.874	0.160	5.519	0.416	0.029	5.931	5.964	**-0.273**
MKB48	2.933	0.271	1.916	0.132	4.639	0.533	0.020	5.253	5.193	**0.574**
MHB49	5.187	0.386	2.196	0.324	7.999	0.018	0.008	8.093	8.025	**0.426**
MSB50	3.568	0.271	1.078	0.300	4.239	0.985	0.031	5.217	5.256	**-0.372**
BOW9	1.815	0.100	1.517	0.112	2.720	0.278	0.217	3.543	3.214	**4.873**
PAW18	3.573	0.090	1.836	0.287	4.559	0.710	0.141	5.786	5.410	**3.356**
BUW21	2.581	0.437	2.196	0.059	4.239	0.228	0.360	5.273	4.827	**4.411**
PUW40	1.867	0.488	1.796	0.072	2.560	1.214	0.082	4.224	3.856	**4.562**
Maximum	7.311	0.488	2.954	0.491	8.399	1.214	0.676	9.847	9.371	**4.873**
Minimum	0.814	0.033	0.878	0.059	1.520	0.018	0.000	2.123	1.976	**-3.194**

Appendix A. 2: Water quality index of water samples

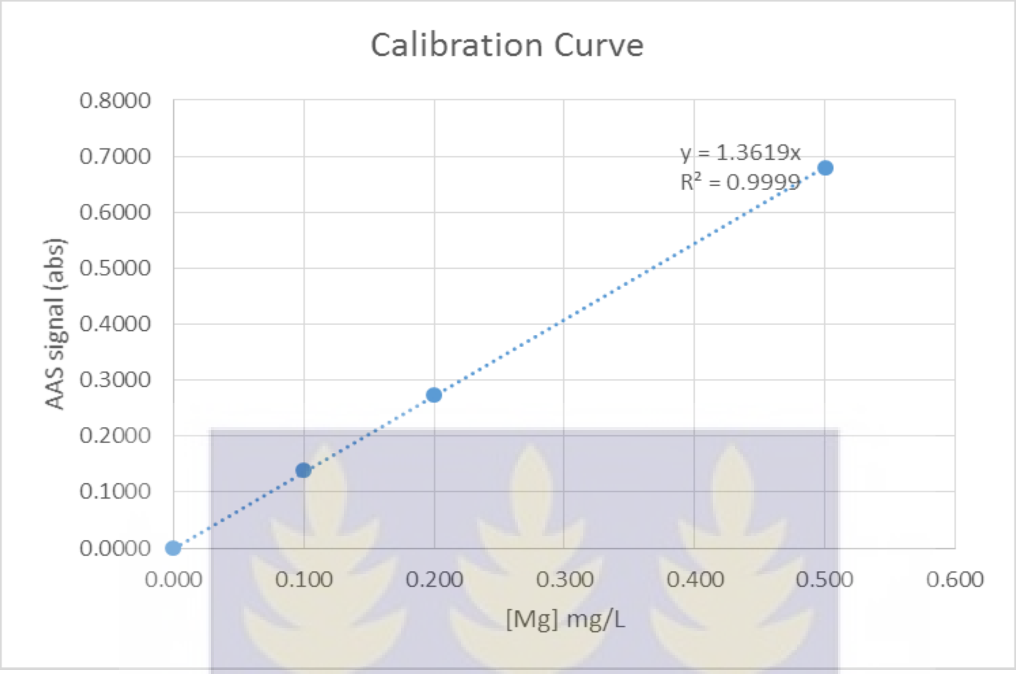
Towns	Site ID	Source	WQI	Description
Pungu	PUB1	Ground Water	8.68	Excellent
Pungu	PUB2	Ground Water	19.18	Excellent
Paga	PAB3	Ground Water	4.43	Excellent
Paga	PAB4	Ground Water	17.72	Excellent
Paga	PAB5	Ground Water	0.47	Excellent
Banyono	BAB6	Ground Water	15.43	Excellent
Banyono	BAS7	Surface Water	57.57	Poor
Boania	BOB8	Ground Water	60.39	Poor
Boania	BOW9	Ground Water	9.95	Excellent
Boania	BOB10	Ground Water	16.48	Excellent
Boania	BOS11	Surface Water	108.48	Unfit for drinking
Nakolo	NAB12	Ground Water	62.88	Poor
Nakolo	NAB13	Ground Water	88.45	Very poor
Nakolo	NAB14	Ground Water	66.33	Poor
Nakolo	NAD15	Surface Water	43.50	Good
Nakolo	SAB16	Ground Water	28.73	Good
Boania	BOS17	Surface Water	19.03	Excellent
Paga	PAW18	Ground Water	43.54	Good
Paga	PAB19	Ground Water	16.60	Excellent
Buru	BUB20	Ground Water	55.23	Poor
Buru	BUW21	Ground Water	4.54	Excellent
Buru	BKB22	Ground Water	12.64	Excellent
Buru	BKB23	Ground Water	87.73	Very poor
Buru	BKS24	Surface Water	11.92	Excellent
Buru	BKS25	Surface Water	56.33	Poor
Navior-Tazika	NTB26	Ground Water	3.05	Excellent
Navior-Tazika	NTB27	Ground Water	0.23	Excellent
Navior-Tazika	NTS28	Surface Water	2134.21	Unfit for drinking
Navior-Tazika	NTB29	Ground Water	5.56	Excellent
Tazika-Batua	TBB30	Ground Water	12.20	Excellent
Tazika-Batua	TBB31	Ground Water	4.04	Excellent
Tazika-Batua	TBB32	Ground Water	10.27	Excellent
Manyoro	MAB33	Ground Water	31.69	Good
Manyoro	MAB34	Ground Water	11.71	Excellent
Manyoro	MAB35	Ground Water	12.04	Excellent
Gomowo	GOB36	Ground Water	20.91	Excellent
Gomowo	GOB37	Ground Water	34.21	Good
Gomowo	GOB38	Ground Water	2.41	Excellent
Pungu	PUS39	Surface Water	28.72	Good
Pungu	PUW40	Ground Water	37.42	Good

Doba	DOS41	Surface Water	9.63	Excellent
Mirigu	MWB42	Ground Water	89.15	Very poor
Mirigu	MWB43	Ground Water	131.30	Unfit for Drinking
Mirigu	MTB44	Ground Water	8.04	Excellent
Mirigu	MNB45	Ground Water	126.31	Unfit for Drinking
Mirigu	MNB46	Ground Water	159.90	Unfit for Drinking
Mirigu	MKB47	Ground Water	109.81	Unfit for Drinking
Mirigu	MKB48	Ground Water	8.27	Excellent
Mirigu	MHB49	Ground Water	54.87	Poor
Mirigu	MSB50	Ground Water	10.26	Excellent
Mirigu	MIS51	Surface Water	58.15	Poor

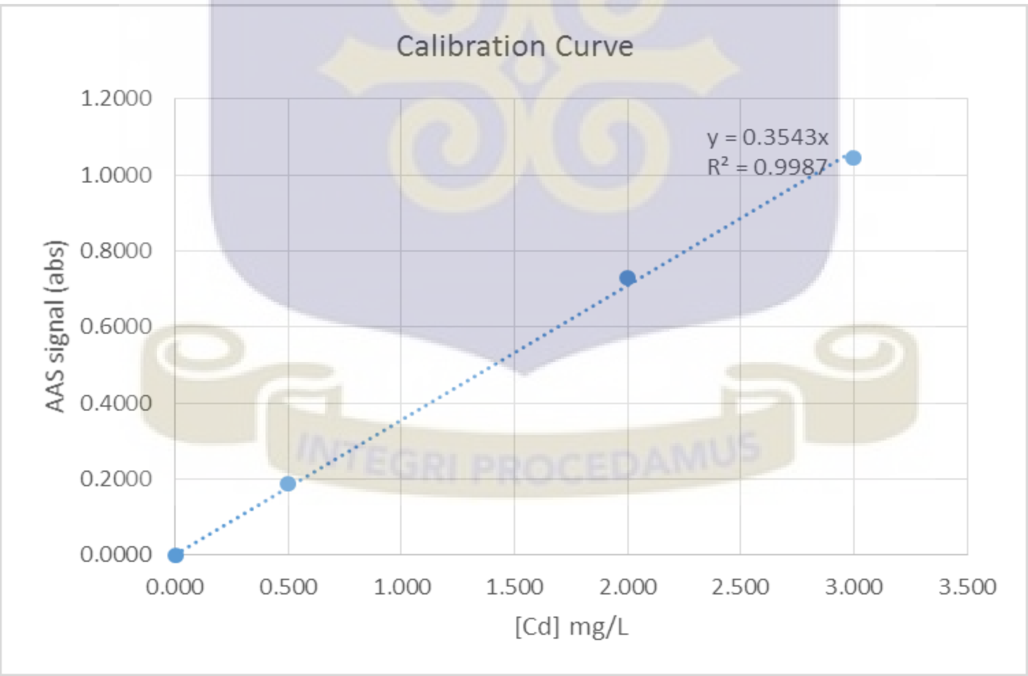
Appendix A. 3: Chloro-alkaline indices of groundwater samples

Towns	**Serial No.**	**Source**	**CAI1**	**CAI2**
Pungu	PUB1	Borehole	-1.52	-0.53
Pungu	PUB2	Borehole	-7.06	-0.55
Paga	PAB3	Borehole	-5.02	-0.43
Paga	PAB4	Borehole	-6.95	-0.57
Paga	PAB5	Borehole	-12.65	-0.46
Banyono	BAB6	Borehole	-13.59	-0.50
Boania	BOB8	Borehole	-33.38	-0.57
Boania	BOW9	Well	-5.89	-0.46
Boania	BOB10	Borehole	-7.20	-0.79
Nakolo	NAB12	Borehole	-14.44	-0.56
Nakolo	NAB13	Borehole	-2.24	-0.33
Nakolo	NAB14	Borehole	-1.56	-0.38
Nakolo	SAB16	Borehole	-20.73	-0.47
Paga	PAW18	Well	-4.16	-0.61
Paga	PAB19	Borehole	-3.87	-0.41
Buru	BUB20	Borehole	-2.95	-0.37
Buru	BUW21	Well	-12.23	-0.57
Buru	BKB22	Borehole	-5.74	-0.51
Buru	BKB23	Borehole	-15.82	-0.53
Navior-Tazika	NTB26	Borehole	-1.72	-0.46
Navior-Tazika	NTB27	Borehole	-10.22	-0.61
Navior-Tazika	NTB29	Borehole	-1.91	-0.50
Tazika-Batua	TBB30	Borehole	-2.35	-0.47
Tazika-Batua	TBB31	Borehole	-1.66	-0.43
Tazika-Batua	TBB32	Borehole	-2.44	-0.54
Manyoro	MAB33	Borehole	-16.65	-0.53

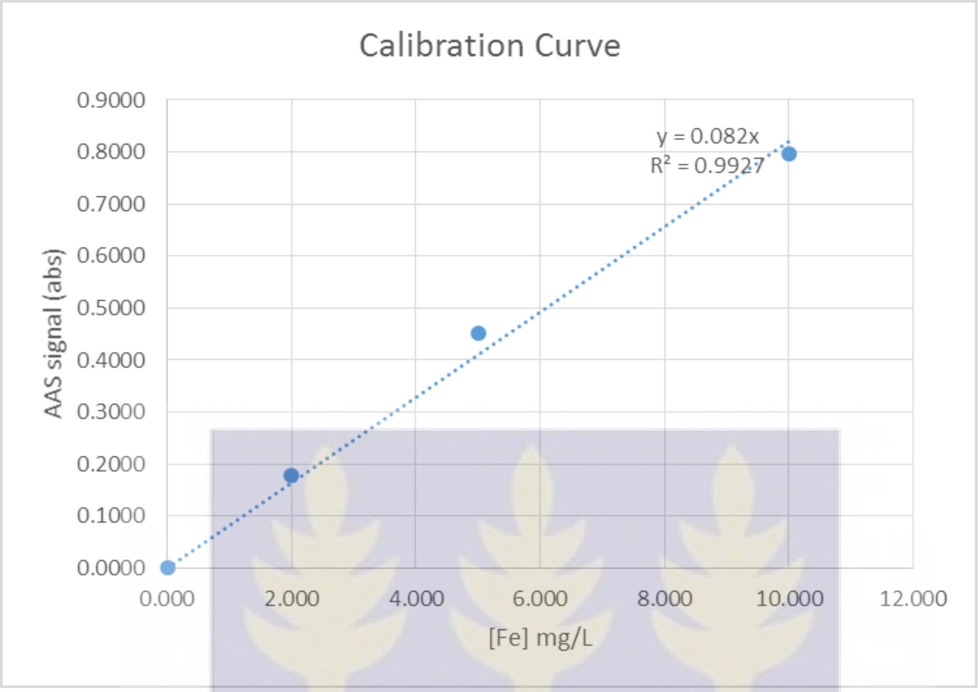
Manyoro	MAB34	Borehole	-10.68	-0.45
Manyoro	MAB35	Borehole	-2.96	-0.43
Gomowo	GOB36	Borehole	-2.16	-0.45
Gomowo	GOB37	Borehole	-13.92	-0.56
Gomowo	GOB38	Borehole	-3.53	-0.52
Pungu	PUW40	Well	-0.94	-0.43
Mirigu	MWB42	Borehole	-3.76	-0.53
Mirigu	MWB43	Borehole	-5.77	-0.50
Mirigu	MTB44	Borehole	-5.30	-0.70
Mirigu	MNB45	Borehole	-10.78	-0.58
Mirigu	MNB46	Borehole	-3.17	-0.52
Mirigu	MKB47	Borehole	-5.97	-0.41
Mirigu	MKB48	Borehole	-5.01	-0.52
Mirigu	MHB49	Borehole	-308.41	-0.64
Mirigu	MSB50	Borehole	-2.90	-0.67



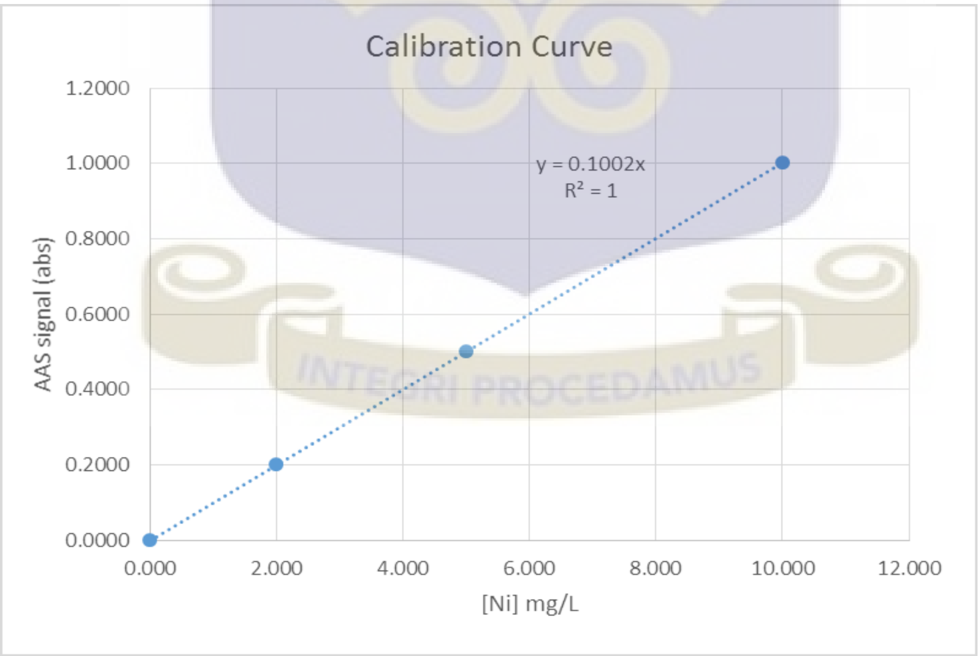
Appendix B. 1: Magnesium (Mg) standards calibration curve



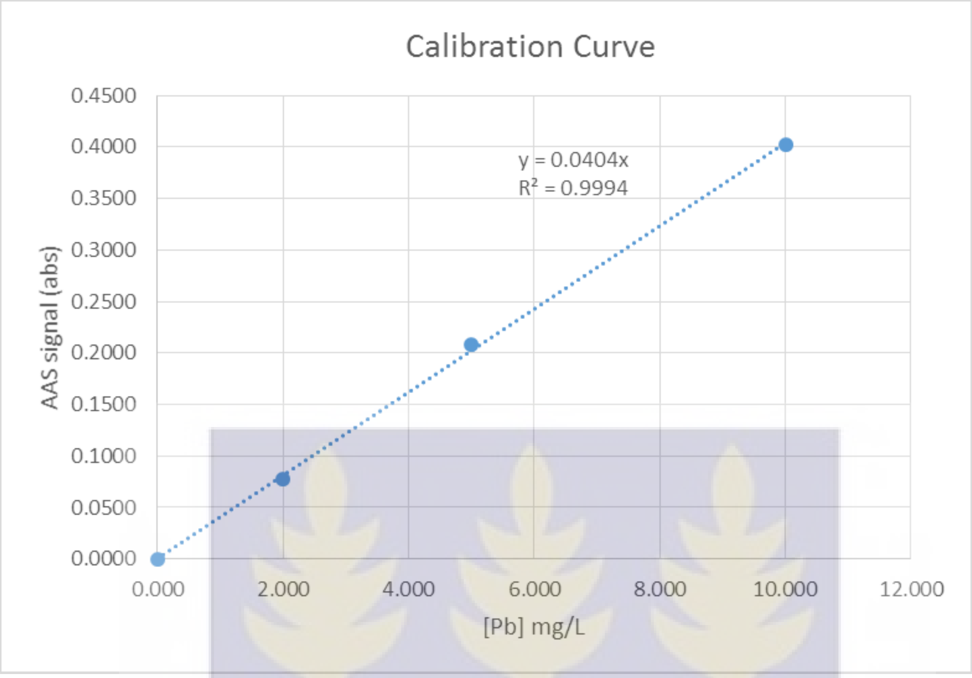
Appendix B. 2: Cadmium (Cd) standards calibration curve



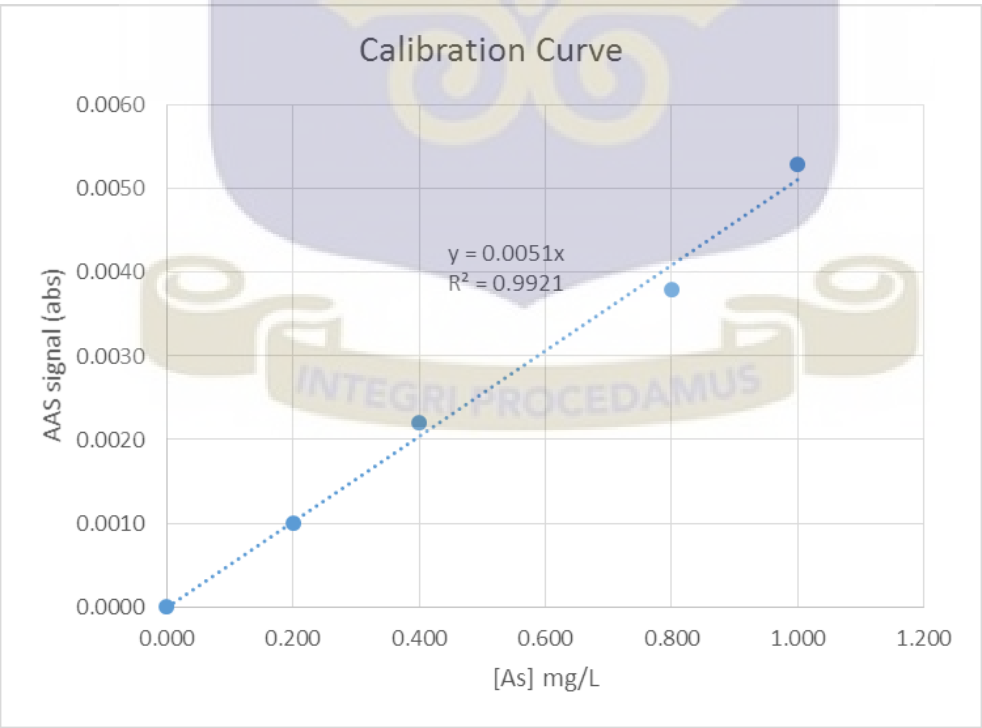
Appendix B. 3: Iron (Fe) standards calibration curve



Appendix B. 4: Nickel (Ni) standards calibration curve



Appendix B. 5: Lead (Pb) standards calibration curve



Appendix B. 6: Arsenic (As) standards calibration curve