CHEMICAL AND ISOTOPIC COMPOSITION OF RAINWATER IN THE COASTAL, FOREST AND MOUNTAINOUS AREAS OF VOLTA REGION OF GHANA

BY

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DECLARATION

I hereby declare that this submission is my own work and that, to the best of my knowledge, it contains no materials previously published by another person or material which has been accepted for the award of any other degree, except where due acknowledgement has been made in the text.

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DEDICATION

This work is dedicated to my two lovely daughters, Princess-Audrey Seyram Djam and Queensly-Hilary Selinam Djam for their patience and inspiration. I love you girls.

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AAS………………….	Atomic Absorption Spectrophotometer
Akiti Line....................	$\delta^2H=7.86\ \delta^{18}O+13.61$
DRWH.......................	Domestic Rainwater Harvesting
EC……………………	Electrical conductivity
EPA…………………..	Environmental Protection Agency
GAEC........................	Ghana Atomic Energy Commission
GHARR 1....................	Ghana Research Reactor 1
GMWL.......................	Global Meteoric Water Line
HPGe..........................	High Power Germanium
IAEA............................	International Atomic Energy Agency
LMWL.........................	Local Meteoric Water Line
LVMWL......................	Lower Volta Meteoric Water Line
MCA...........................	Multichannel Analyser
MDG...........................	Millennium Development Goal
NAA............................	Neutron Activation Analysis
NGO............................	Non Governmental organization
NNRI...........................	National Nuclear Research Institute
OA-ICOS.....................	Off-axis Integrated Cavity Output Spectroscopy
TDS…………………..	Total dissolved solids
TSS…………………...	Total suspended solids
TWDB.........................	Texas Water Development Board
VSMOW……………..	Vienna Standard Mean Ocean Water
WHO…………………	World Health Organization
WQI…………………	Water Quality Index

ABSTRACT

Harvesting rainwater for domestic use is one of the oldest technologies developed by man. In Ghana, groundwater utilization challenges posed by dry wells and high levels of contaminants such as iron, fluoride and other minerals in some geological formations makes harnessing of rainwater for household use inevitable. Whiles researchers are looking for efficient ways of dealing with contaminants associated with these water sources, focus is gradually shifting to the development of enhanced methods for rainwater harvesting. In this study, rainwater samples were collected from Akatsi (a coastal zone), Amedzofe (high altitude zone) and Kpando (a forest zone) in the Volta region of Ghana and analyzed for the physico-chemical parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), colour, turbidity, alkalinity, Ca^{2+}, K^{+}, Na^{+}, Mg^{2+}, NO_3^-, NH_4^+, pH, Cl^-, and SO_4^{2-}. The results showed that, pH values of the Akatsi, Amedzofe and Kpando rainfall ranges from 5.40 to 6.85, 4.3 to 6.3 and 4.76 to 6.00 respectively. Amedzofe showed a relatively low pH with 13.70% ranging from 4 to 5, 82.40% of the rainfall events fell within pH of 5 to 6 and 3.90% had pH less than 7 but greater than 6. About 96.10% of the total rainfall events had pH less than 6. EC, TDS, turbidity and colour were generally low with higher values recorded at Akatsi while Amedzofe recorded the lowest values. The concentration of major ions and element-to-sodium ratios showed clear variations with higher levels found in Akatsi (coastal zone) and lower levels found in Amedzofe. Anion order of dominance in Akatsi, Kpando and Amedzofe are $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$, $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^-$ and $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ respectively, while cation order of dominance are $Na^+ > Mg^{2+} > Ca^{2+}$, $Ca^{2+} > Na^+ > Mg^{2+}$ and $Na^+ > Ca^{2+} > Mg^{2+}$ for Akatsi, Amedzofe and Kpando respectively. Isotopic composition of rainwater was also determined for the three areas. Akatsi (coastal zone) presents high values of $\delta^{18}O$

and δ^2H, whereas rainwater in Amedzofe was characterized by low values of $\delta^{18}O$ and δ^2H, Kpando on the other hand was intermediately high. The Local Meteoric Water Line for the study area using rainfall greater than 20mm was defined as $\delta^2H = 7.453\ \delta^{18}O + 8.621$ ($n=45$; $R^2=0.907$, rain > 20mm). Isotope fractionation in precipitation, including depletion in both $\delta^{18}O$ and δ^2H is primarily due to the rainout and the altitude effects with temperature effect being insignificant. The calculated altitude effect shows a gradual lapse rate of $\delta^{18}O$ and $\delta\ ^2H$ of about -0.2‰/100 m and -1.5 ‰/100 m for Akatsi and Amezofe respectively. Amedzofe and Kpando showed an altitude effect of -0.15‰ /100 m. and -2 ‰/100 m for $\delta^{18}O$ and δ^2H respectively. The groundwater in the study area is mainly of meteoric origin with different months of recharge. The plot of $\delta^{18}O$ and EC shows that, mineral dissolution is the main factor controlling the groundwater salinization in Akatsi while Amedzofe and Kpando groundwater chemistry are mainly controlled by evaporation.

CHAPTER ONE

1.0 INTRODUCTION

Water is one of the most important commodities for the sustenance of life; consequently, clean and fresh water is vital for the wellbeing of the human society. Many living organisms use water as their habitat.

In Ghana, as in many areas, surface water and groundwater constitute the main source of water for domestic, industrial and agricultural uses. Water scarcity and pollution problems have generated public discussions and concerns by both policy makers and researchers. This has lead to several studies on the quality of groundwater and surface water in Ghana using conventional methods (Kortatsi, 1998, Fianko et al., 2008, Adomako et al., 2010 etc).

In recent years, however, stable isotopes were used as complementary tools to study the origin and mixing pattern of groundwater (Akiti, 1980; Acheampong and Hess, 2000; Adomako et al., 2010, Gibrilla et al., 2010), groundwater recharge (Adomako et al., 2010). However, these studies did not have enough information on the input function (oxygen-18 and deuterium), which were scarce on precipitation composition.

Ghana records about 40 billion cubic meters of rainfall annually which is equal to nine trillion gallons of water (Ministry of Water Resources, Works and Housing).http://www.ghanabusinessnews.com/2011/07/19/.

Ghana therefore, has a great potential for rainwater harvesting for domestic use. Several households in urban and peri-urban communities harvest and store rainwater in small water storage containers. The technology has developed further to include construction of large concrete reservoirs for schools, health centers, churches and agricultural purposes.

Atmospheric precipitation is one important part of the natural water cycle that plays a significant role in carrying chemical pollutants from the atmosphere to the earth's surface. Water-soluble inorganic ions (Mg^{2+}, K^{+}, Ca^{2+}, Na^{+}, Cl^{-}, NO_3^{-}, etc) constitute a significant portion of total particulate matter and precipitation samples and thus have direct and indirect impacts on air quality, climate and ecosystems. To address various issues related to these ions, their concentrations in air and in precipitation, the sources and chemical mechanisms producing those ions need to be understood at local, regional, and global scales.

To date, many studies around the world have revealed the source types, formation mechanisms, chemical and physical characteristics, and dry and wet deposition of the major water-soluble inorganic ions (Zhang et al.,2007), Chemical characteristics of precipitation and Sulfate formation in atmospheric ultrafine particles, (Tu et al.,2005).

However, studies in the area are still limited. Volta Region has countless number of migrants from its neighbouring countries, Togo and Nigeria to the East which has an increase effect in the population.

Increased aerosol concentrations (sea and fumes from vehicle and industries) have a strong impact on air/water quality. Removal of gases and aerosol by clouds and precipitation, as in-cloud (rainout) and below-cloud (washout) processes, play an important role in determining the distribution and concentration of pollutants in the atmosphere (Feng et al.,2001; Tang et al., 2005). The formation of clouds relies on the presence of aerosol particles, which act as cloud condensation nuclei, and heterogeneous nucleation of water vapour leads to dissolution of the soluble materials contained within the cloud condensation nuclei. These soluble materials comprise with the initial chemical compositions of newly formed cloud droplets, rainfall.

Precipitation geochemistry results from a complex series of interactions between cloud dynamics, microphysical processes, and a series of rainout and washout chemical reactions in the atmosphere (Desboeufs et al., 2010).

Even though in Ghana, stable isotopes of rain water ($\delta^{18}O$, $\delta^{2}H$) have been fairly assessed (Akiti, 1980), data on rain water quality and chemical composition in Ghana is scarce. Most studies involving stable isotopes of water are based to a large extent on groundwater and surface water resources. Akiti (1980) and Armah (2000) employed $\delta^{18}O$ and $\delta^{2}H$ to study the salinization of groundwater in parts of southern Ghana (Accra plains). Stable isotope results showed no relationship between the groundwater system and possible seawater intrusion. Kortatsi (2006) employed chemical and isotopic tools to characterize and identify the origin of salinity in the Accra plains of Ghana. Acheampong and Hess (2000) used stable and radioactive isotopes to investigate the source of recharge and the age of the shallow groundwater system within the southern Voltaian sedimentary basin of Ghana. Generally, low tritium concentrations in the groundwater samples were found in the range less than 1 to 7.2 TU and useful in the identification of modern recharge. JØrgensen and Banoeng-Yakubo (2001) applied environmental isotopes (^{18}O, ^{2}H, and $^{87}Sr/^{86}Sr$) in groundwater with emphasis on saline groundwater aquifers in the Keta basin of Ghana and discovered that ground waters from deep and dug wells in coastal aquifers are characterized by relatively high chloride contents, and marine influence is evidenced by well-defined mixing line for strontium isotopes, hydrogen and oxygen stable isotopes with similar isotopic compositions of seawater.

Stable isotopes of water have also been used to investigate wetlands, to understand their hydrological processes notably recharge and origin in the White Volta River Basin, Densu Delta and Sakumono wetlands, under International Atomic Energy

Agency (IAEA) Coordinated Research Projects (Adomako et al., 2010) used $\delta^{18}O$ and $\delta^{2}H$ to estimate mean recharge rates into the groundwater system of the Densu river basin as 110 to 250mm/year representing about 8% of annual rainfall.

The combination of chemical data with stable isotope ($\delta^{18}O$ and $\delta^{2}H$) data in precipitation has proven to be a useful tool for; exploring the relationship between the origins of air masses, precipitation characteristics (Craig, 1961; IAEA, 1980; Prathibha et al., 2009), distinguishing the different sources that contribute to rainwater chemistry (Tuncel and Ungor, 1996; Yamanaka et al., 2007).

This work, therefore, seeks to explore the relationship between chemical and isotopic data of rainwater in Akatsi (coastal), Amedzofe (Mountainous) and Kpando (forest) in the Volta region of Ghana.

Trace elements in the rainwater samples were also analysed using instrumental neutron activation analysis with the objective of identifying the essential trace elements for life or health and to investigate the migration of chemical species and the distribution of these trace elements derived from pollution.

Rainwater is the natural primary input or natural recharge of groundwater and surface water (Ganyaglo 2009). The process of recharge is very complicated, thus one of the most important factors is the time delay between the time when the meteoric water enters the soil profile, and the time when it is manifested as an effectively exploitable groundwater source.

The actual recharge rate is control by several factors including the amount and the rate of rainfall not lost to surface runoff and evapotranspiration, (Leap,1999).

This therefore implies that there is a need to investigate the interaction of rainwater–groundwater in the study area; hence, this study will also attempt to explore the relationship between the groundwater and rainwater in the study area.

1.1 OBJECTIVES

The aim of this study is to understand the chemical composition of rain water collected from three (3) zones in the Volta Region and also to identify the severity of threats due to expanding industries on the physical, chemical and stable isotope composition of the rainwater.

Other specific objectives include;

- To identify the origin of solutes in rainwater and determine the rainwater quality.
- To characterize the rainwater cycle by comparing my data with isotopic results from surrounding areas
- To investigate the partial pattern of rainfall changes and possible causes thereof and the seasonal variation of stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) in the three major areas.
- To investigate continental effect, amount effect and altitude effect.
- To investigate the interaction between rainwater and groundwater.

1.2 STATEMENTS OF THE PROBLEM

In Ghana and the Volta region in particular, most of the agricultural activities, about 90-98% depend on rainwater. Small and peri-urban communities are increasingly accepting rainwater harvesting as a technology choice capable of meeting their water demands for domestic activities. However, little knowledge of the rainwater quality, chemical composition and sources of solute deposits in the rainwater of the area are known. Hence, the spatial and temporal variations in the rainfall chemistry of these regions are not clearly understood.

The stable oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) isotopic compositions of water are widely used as tracers to study the global hydrological cycle. Various researchers have observed that heavy isotopes in rainfall and snow vary widely and predictably across the globe, providing a finger print or label incorporated in climate archives such as ice cores, lake sediments, corals, tree rings, limestone caves and groundwater, (Ichiyanagi 2007; Wooller 2007; Clark and Fritz, 1997).

The patterns of isotopes in precipitation are the result of global and local meteorological processes. These isotopes therefore serve as ideal hydrological tracers and have been applied to study past climate, paleohydrology, wildlife migration, archaeology and forensics. Ichiyanagi (2007) stated that stable isotopes in precipitation ($\delta^{18}O$, $\delta^{2}H$) contain information on both the origins of precipitation and its transport because heavy and light isotope species undergo different fractionation during phase changes.

1.3 JUSTIFICATION

As a vital natural resource, water is fundamental for the sustainable development of the economy, the ecosystem, and biodiversity. Therefore, water security and related implications for ecosystem and river diversity, especially the variability and availability of regional water resources under the influence of climatic change and human activities are warmly discussed in recent years (Xu and Singh, 2004).

Nevertheless, it is being increasingly recognized that water resources are deteriorating in many parts of the world. While researchers are looking for efficient ways of dealing with contaminants associated with these water sources, challenges posed by dry wells, as well as excessive levels of contamination especially minerals in the groundwater resources of some geological formations makes harnessing of rainwater for household use unavoidable.

If rainwater resources are managed well, emerging phenomena like flooding and erosion in our communities could be contained. The resource if properly harnessed has benefits, which would contribute to meeting our millennium development goals (MDG) on water and environmental sanitation by year 2015.

Precipitation being the primary input to surface water and groundwater systems; most of the studies provide little information on the chemical and stable isotope composition of rainwater in Ghana (Apraku A and Adu-Kumi M, 2014; Cobbina et al.,2013; Akoto et al., 2011).

The study area shares boundary in the coast with the heavy industrial city of Ghana, Tema and there might be severe threats these expanding industries may have on rainwater with accompanying chemical deposits. Therefore for sustainable water resource planning and management, adequate hydrological data and information on rainfall patterns, availability of water within the catchment area should be investigated. There is therefore the need for a comprehensive study of rainwater in this region that will combine chemical and isotopic indicators.

CHAPTER TWO

2.0 LITERATURE REVIEW

In this Chapter an extensive literature has been reviewed in the areas of; water supply in the Volta region of Ghana, rainwater harvesting and storage, rainwater quality including stable isotopes in hydrology and hydrological cycle.

2.1 WATER SUPPLY IN THE VOLTA REGION OF GHANA

Water as a valuable natural resource, sustains the environment and supports livelihood. However, access to potable water is still a challenge to many developing countries. WHO (1997) estimated about 1.2 billion people in developing countries are without access to "safe water" and a further 2 billion lack adequate sanitation. Many rural communities in Ghana depend on rivers, streams, hand dug-wells, boreholes and rainwater for their water needs (Zakaria Issaka, 2011). Most of these water supply sources especially the surface waters are increasing under threat of pollution and serve as the main sources of water-borne and water-related diseases (Gyau-Boakye and Dapaah-Siakwan, 1999). About 70 % of diseases in Ghana are currently linked to insufficient water supply and sanitation issues (IFFM, 2002).

In the Volta region of Ghana, several efforts by the government and other Non-governmental organizations were made to provide potable water to the communities, (Danida, 2003). Following water resources sector studies that were commissioned by the Government of Ghana in 1969–1970, it became the official policy that for the supply of potable water, communities below 500 inhabitants are to be helped in the construction of hand-dug wells, (Mensah, 1998). Communities between 500 and 2,000 in population are supplied by hand-dug wells or boreholes fitted with hand pumps, whereas communities of population between 2,000 and 5,000 are supplied with pipe-borne systems. While some of these pipe-borne systems have surface water sources, most of them are based on groundwater resources. Where these technologies are not feasible, rain catchment, spring sources, and surface water from dams are used. Those communities that have not yet benefited from these policies still rely on the traditional sources for their water supply needs. These sources include dug wells, ponds, dugouts, springs, ephemeral streams, and rainwater harvesting.

2.1.1 GROUNDWATER AND SURFACE WATER

Groundwater occurs almost everywhere beneath the earth surface not in a single widespread aquifer but in thousands of local aquifer systems and compartments that have similar characters (Moore, 2002; Banoeng-Yakubo, 2007). Knowledge of the occurrence, replenishment, and recovery of groundwater has special significance in arid and semi-arid regions due to discrepancy in monsoonal rainfall, insufficient surface waters and over drafting of groundwater resources (De Vries and Simmers, 2002).

The quality of groundwater depends on the quality of recharged water, atmospheric precipitation, inland surface water, and on sub-surface geochemical processes, (Appelo and Postma, 1993). Temporal changes in the origin and constitution of the recharged water, hydrologic and human factors, may cause periodic changes in groundwater quality.

Several studies on groundwater in the coastal area of the Volta region especially the Keta basin exist in literature. Kortatsi et al., (2006) studied potential impact of large-scale groundwater abstraction on the shallow groundwater and on crop production within the Keta Strip using geophysical and hydrochemical data. The study revealed that, shallow groundwater can support only medium to high salt tolerant crops such as shallot and onions. The study further postulated that, abstraction of large volume of water from the shallow aquifer will result in the lowering of water table by approximately 1.0 m per year. The consequence of this will be the up coning of the fresh/saline water interface probably by as much as 4.7 m, resulting in salinisation of the fresh water lenses particularly around the lagoon end where most of the shallot farms are situated. The author further stated that, even though, post irrigation rainfall will be adequate to nullify the water table depression, once the fresh water is contaminated, it is extremely difficult to decontaminate. Consequently, the shallow groundwater will evolve from medium through high to very high salinity hazard to crops. Specific ions toxicity will also increase due to increment in the concentrations of individual ions. Thus, the previously freshwater system will become unsuitable for the production of even high salt tolerance crops. This will effectively halt the lucrative shallot and other vegetable farming in the Keta Strip and thus signify socio-economic disaster for the Keta Strip in particular and Ghana in general.

Yidana et al., (2007) also studied groundwater in the Keta basin and concluded that, despite the threat of sea water intrusion, the groundwater is suitable for irrigation without adverse effect on soil hydraulic properties. Later in 2010, studies by Yidana et al., (2010) on the quality of groundwater in the Keta basin using Water Quality Index (WQI) categorized the groundwater as good, fair and marginal.

Earlier studies on the origin of groundwater in the Keta basin using stable isotopes by Akiti (1977), Bannerman (1994), Nerquaye-Tetteh (1993) postulated a hydraulic connectivity between limestone aquifer and Mono River. A much later study by Helstrup (2006) using δ^2H and $\delta^{18}O$ composition of groundwater from the limestone aquifer in the Coastal Sedimentary Basin of Togo does not show any influence of evaporation, which excludes the hypothesis, suggested in previous studies (Akiti, 1977; Bannerman, 1994; Nerquaye-Tetteh, 1993). However, all these studies confirmed the existence of old groundwater in the basin of up to 15000 years.

However, in the Akatsi district which forms part of the study area, only few studies on groundwater exist. Tay (2006) studied the chemical characteristics of groundwater in the Akatsi districts by collecting water samples from 34 boreholes. The results revealed that groundwater in the district are soft but slightly acidic with pH values ranging from 5.75 –7.39. Groundwater in the district was also found to be mineralized with conductivity ranging from 170 – 6440 µS/cm. He concluded that, NO_3-N, SO_4^{2-} and Cl^- ion concentrations in some boreholes in the district was at such elevated levels that serious health effects and risks might arise after prolonged and continuous use. This establish the fact that groundwater in the study area has high contamination level due to agricultural practices and improper sanitation.

The results of these analyses point to a future threat to groundwater supply in the area due to increasing water quality deterioration. This is shown by the high electrical conductivity (EC) values. However, groundwater studies and data in the forest (Kpando) and mountainous (Amedzofe) are scarce.

Rivers, streams, springs, lakes and ponds mainly constitute surface water in the study area. The forest area is mainly dominated by the River Volta, the mountainous areas by network of springs while the coastal area is dominated by rivers and some ephemeral streams. These water sources are heavily polluted with faecal matter from the communities along the water sources and chemical deposits from agricultural practices.

2.1.2 RAINWATER

Rain is liquid water in the form of droplets that have condensed from atmospheric water vapour and then precipitated (become heavy enough to fall under gravity). Rain is a major component of the water cycle and is responsible for depositing most of the freshwater on the Earth. It provides suitable conditions for many types of ecosystems, as well as water for hydroelectric power plants and crop irrigation (Vörösmarty et al., 2010).

The major cause of rain production is moisture moving along three-dimensional zones of temperature and moisture contrasts known as weather fronts. If enough moisture and upward motion is present, precipitation falls from convective clouds (those with strong upward vertical motion) such as cumulonimbus (thunder clouds) which can organize into narrow rain bands. In mountainous areas, heavy rainfall is possible where upslope flow is maximized within windward sides of the terrain at elevation which forces moist air to condense and fall out as rainfall along the sides of mountains. On the leeward side of mountains, desert climates can exist due to the dry air caused by down slope flow which causes heating and drying of the air mass (Dai, 2006). The movement of the monsoon trough, or intertropical convergence zone, brings rainy seasons to savannah climes.

The urban heat effect leads to increased rainfall, both in amounts and intensity, downwind of cities. Global warming causes change in the precipitation pattern globally, including wetter conditions across Eastern North America and drier conditions in the tropics with Antarctica being the driest continent (Arnell, 1999; Alan et al., 2003). The globally averaged annual precipitation over land is 715 mm (28.1 in), but over the whole Earth it is much higher at 990 mm/ 39in (Kottek et al. 2006). Climate classification systems such as the Köppen-Geiger climate classification system use average annual rainfall to help differentiate between differing climate regimes. Rainfall is measured using rain gauges. Rainfall amounts can be estimated by weather radar.

2.1.2.1 FORMATION OF RAINWATER

Air contains water vapour and the amount of water in a given mass of dry air, known as the mixing ratio, is measured in grams of water per kilogram of dry air (g/kg) (Kempler 2009). The amount of moisture in air is also commonly reported as relative humidity; which is the percentage of the total water vapour air can hold at a particular air temperature. How much water vapour a parcel of air can contain before it becomes saturated (100% relative humidity) and forms into a cloud (a group of visible and tiny water and ice particles suspended above the Earth's surface) depends on its temperature (Glossary of Meteorology, June 2000). Warmer air can contain more water vapour than cooler air before becoming saturated. Therefore, one way to saturate a parcel of air is to cool it.

There are four main mechanisms for cooling the air to its dew point (this is the temperature to which a parcel must be cooled in order to become saturated): adiabatic cooling, conductive cooling, radiational cooling, and evaporative cooling (Mark, 2005).

Adiabatic cooling occurs when air rises and expands. The air can rise due to convection, large-scale atmospheric motions, or a physical barrier such as a mountain (orographic lift). Conductive cooling occurs when the air comes into contact with a colder surface, usually by being blown from one surface to another, for example from a liquid water surface to colder land. Radiational cooling occurs due to the emission of infrared radiation, either by the air or by the surface underneath. Evaporative cooling occurs when moisture is added to the air through evaporation, which forces the air temperature to cool to its wet-bulb temperature, or until it reaches saturation (Fovell, 2004).

The main ways water vapour is added to the air are: wind convergence into areas of upward motion, precipitation or virga falling from above, daytime heating evaporating water from the surface of oceans, water bodies or wet land, transpiration from plants, cool or dry air moving over warmer water, and lifting air over mountains. Water vapour normally begins to condense on condensation nuclei such as dust, ice, and salt in order to form clouds. Elevated portions of weather fronts (which are three-dimensional in nature) force broad areas of upward motion within the Earth's atmosphere which form clouds decks such as altostratus or cirrostratus (Pidwirny 2007; FMI (2007).

2.1.2.2 RAINWATER HARVESTING AND STORAGE

Rainwater harvesting is considered as the oldest technology developed by man to provide potable water for domestic use (Boers and Ben-Asher,1982). In Africa, rainwater harvesting projects have increased in recent years due to the increased number of polluted or dried-out boreholes and wells or neglected water supplies in rural communities (Gould and Nissen-Petersen, 1999). Although rainwater harvesting is gaining popularity in sub-Saharan Africa, it faces some challenges. First, rapid population growth in urban areas accompanied by increase in industrialization leading to release of pollutants into the atmosphere such as chemical contaminants may dissolve during rainfall and also microbial risks can be introduced through bird droppings. Second, the roof types and sizes of many rural houses are not suitable for rainwater harvesting and can compromise the system's efficiency and even the quality of water. Lastly, due to high installation and storage costs, low income households are more likely to invest in materials that are within their budgets and not those that are optimum for the system (Thomas, 1998).

The technique was later developed to cover the collection of run off for agricultural purposes and installation of large reservoirs that are used to regulate flooding, in some developed countries such as Japan, (Mooyoung, 2004).

In Ghana, rainwater harvesting started at the household level where small water storage containers are used to collect and store rainwater during storms. Currently, the technology has developed further to include construction of large concrete reservoirs for schools, health centers and churches. Storage tanks are the most expensive part of Domestic Rainwater Harvesting System and may be located above or below the ground (Lundgren and Akerberg, 2006). Storage tanks are installed to make for later use of water and aid self-sufficiency. The size of rainwater tank is dictated by the rainwater supply, water demand, and length of dry spell, the roof surface area, aesthetics, personal preference, and budget (TWDB, 2005). The cost of rainwater tanks depends on size, make, installation, additional fittings and supplies. There are many types of rainwater storage containers in different geographical regions. Earthenware cisterns, large pots, metal and plastic drums.

Polyethylene tanks are relatively inexpensive and durable, lightweight, and long lasting. Polyethylene tanks are available in capacities from 50 - 15,000 gallons. Rainwater collected and stored in plastic water tanks remains naturally acidic and can react with the copper pipes that carry the water to household taps (TWDB, 2005). The naturally acidic rainwater can corrode the copper pipe which causes gastric problems and headaches, and in severe cases cirrhosis of the liver. A bag of limestone chips are added to a plastic tank to make the water alkaline.

Metal tanks are also available in sizes from 150 - 2,500 gallons, and are lightweight and easy to relocate (TWDB, 2005). Most metal tanks are corrugated galvanized steel dipped in hot zinc for corrosion resistance. They can be lined with polyethylene or coated inside with epoxy paint.

The other most commonly used storage tank is the concrete tanks. The Concrete is a composite material consisting of a cement binder in which an inert aggregate is embedded. One advantage of concrete tanks is their ability to decrease the corrosiveness of rainwater by allowing the dissolution of calcium carbonate from the walls (Lundgren and Akerberg, 2006). Cement is subject to deterioration on prolonged exposure to aggressive water, due to the dissolution of lime or chemical attack by aggressive ions such as chloride or sulfate, and this may result in structural failure.

2.1.2.3 RAINWATER QUALITY

Rainwater is relatively free from impurities except those scavenged by rain from the atmosphere, but the quality of rainwater may deteriorate during harvesting, storage and household use (Polkowska et al., 2001). Wind-blown dirt, leaves, faecal droppings from birds and animals, insects and contaminated litter on the catchment areas can be sources of contamination of rainwater, leading to health risks from the consumption of contaminated water from storage tanks. Poor hygiene in storing water in and abstracting water from tanks or at the point of use can also represent a health concern. However, risks from these hazards can be minimized by good design and practice. Well designed rainwater harvesting systems with clean catchments and storage tanks supported by good hygiene at point of use can offer drinking-water with very low health risk, whereas a poorly designed and managed system can pose high health risks.

Microbial contamination of collected rainwater indicated by *E. coli* (or, alternatively, thermotolerants coliforms) is quite common, particularly in samples collected shortly after rainfall. Pathogens such as *Cryptosporidium*, *Giardia*, *Campylobacter*, *Vibrio*, *Salmonella*, *Shigella* and *Pseudomonas* have also been detected in rainwater (Brodie et al 2006). However, the occurrence of pathogens is generally lower in rainwater than in unprotected surface waters, and the presence of non-bacterial pathogens, in particular, can be minimized (Chang and Crowley, 1993).

Higher microbial concentrations are generally found in the first flush of rainwater, and the level of contamination reduces as the rain continues (Kingett Mitchell, 2003). A significant reduction of microbial contamination can be found in rainy seasons when catchments are frequently washed with fresh rainwater. Storage tanks can present breeding sites for mosquitoes, including species that transmit dengue virus.

Rainwater is slightly acidic and very low in dissolved minerals; as such, it is relatively aggressive. Rainwater can dissolve heavy metals and other impurities from materials of the catchment and storage tank. In most cases, chemical concentrations in rainwater are within acceptable limits; however, elevated levels of zinc and lead have sometimes been reported (Quek and Förster, 1993). This could be from leaching from metallic roofs and storage tanks or from atmospheric pollution.

Rainwater lacks minerals, but some minerals, such as calcium, magnesium, iron and fluoride, in appropriate concentrations are considered very essential for health. Although most essential nutrients are derived from food, the lack of minerals, including calcium and magnesium, in rainwater may represent a concern for those on a mineral-deficient diet. In this circumstance, the implications of using rainwater as the primary source of drinking-water should be considered. The absence of minerals also means that rainwater has a particular taste or lack of taste that may not be acceptable to people used to, drinking other mineral-rich natural waters.

Hydrochemistry study of rainwater is an important aspect for drinking, irrigation and industrial purposes. Hydrochemistry application has been used to help define the chemistry of waters in areas all over the world. The chemical composition of rainwater has a direct linkage on the quality which also has important implications on health and environment (Peterson et al, 1971).

The importance of water quality in human health has recently attracted a great deal of interest. In the developing world, 80% of all diseases are directly related to poor drinking water and unsanitary conditions (Olajire & Imeokparia, 2001). Rainwater contains many chemicals and each has its importance and for that matter the acceptable concentration levels. The chemical composition of rainwater has a direct bearing on the quality and the factors that influence the quality of groundwater in a particular basin and can be diverse and varied. Physical parameters such as pH, TDS, Salinity and Conductivity and chemical parameters such as Cl^-, NO_3^-, SO_4^{2-}, HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, are normally used to ascertain the quality of the water.

2.1.2.4 RAINWATER QUALITY STUDIES IN GHANA

Despite the over emphasis on groundwater and surface water studies in Ghana, few studies exist for rainwater quality. Bhavananda (2010) studied the potential of rain water harvesting in Ayigya a suburb of Kumasi. The studies focused on the techno-financial feasibility of adopting rain water harvesting in the most cost-effective way at household level. The work revealed that rooftop rain water harvesting is a techno-financially viable option considering the perception of the various stakeholders and the availability of various building components suitable for adopting the system at household level.

Osei Asare (2004) worked on Household Water Security and Water Demand in the Volta Basin of Ghana. Barnes (2009) assessed the current state of rainwater harvesting in the Northern Region of Ghana and makes recommendations regarding it and how rainwater harvesting could be used to address Pure Home Water's goal of reaching 1 million people in the next five years with safe drinking water. Anna et al., (2006) researched on rainwater harvesting in the peri-urban areas of Accra: It's status and prospects and concluded that the peri-urban areas of Accra are appropriate for Domestic Rainwater Harvesting (DRWH), but only as a complementary source of water supply.

Issaka, (2011) studied appropriate rainwater harvesting and domestic water quality a case study of central Gonja district and recommended rainwater generally for drinking, cooking, bathing and washing for the people of Central Gonja district.

Apraku and Adu-Kumi, (2013) assessed the physico-chemical and bacteriological parameters of rain water in Adukrom-Akwapim where heavy rain falls were experienced during the wet season. Direct rainfall, stored rainwater and roof catchment rainwater were sampled and studied. The result showed a significant increase in physico-chemical and bacteriological parameter from the direct rainfall to roof catchment and the stored rainwater. They suggest a form of treatment before use for drinking.

Akoto et al., (2011) carried out a comprehensive study on the chemical composition of rainwater in Obuasi a mining community in Ghana. The rain water in Obuasi was found to be acidic (4.0 to 5.6). The rainwater chemistry in the area was found to be strongly influenced by the local anthropogenic activities in the area (mining) with Lead (Pb) found to be above the WHO permissible limit of 0.01mg/l for drinking water.

2.2 PHYSICAL PARAMATERS

2.2.1 pH

The pH is an important variable in water quality assessment as it influences many chemical and biological processes within a water body and all processes associated with water supply and treatment. The pH is a measure of the acid balance of a solution and is defined as the negative of the logarithm to the base 10 of the hydrogen ion concentration (Butler, 1964). The pH scale runs from 0 to 14 (i.e. very acidic to very basic), with pH 7 representing a neutral condition. At a given temperature, pH (or the hydrogen ion activity) indicates the intensity of the acidic or basic character of a solution and is controlled by the dissolved chemical compounds and biochemical processes in the solution (Chapman, 1996). Water undergoes slight dissociation into hydrogen ions (H^+) and hydroxyl ions (OH^-). When the concentrations of these two ions are equal, the solution is considered neutral. If the concentration of hydrogen ions is larger than the concentration of hydroxyl ions, the solution is acidic. If hydroxyl ions are in greater concentration, the solution is considered basic.

The acidity of water is generally expressed by concentration of hydrogen and hydroxyl ions in solution, (in moles per litre). Knobel et al., (1988) observed that pH can be affected by the presence of other species that controls the water types, for instant predominantly calcium-magnesium bicarbonate water have low dissolved solids content and low pH near outcrop recharge areas while predominantly sodium bicarbonate water types have high dissolved solids content and high pH, down gradient. A high aluminium concentration also has the propensity of reducing the acidity level because the Al can undergo hydrolysis to give excess hydroxonium ions (OH^-). Kortatsi (2006) observed that boreholes with pH in the basic region are associated with high Al, As, Mn, Fe, and Hg with concentrations significantly above their respective detection limits in the Ankobra Basin. Low pH values of rainwater might also be as a result of other factors that are anthropogenic or extreme natural conditions. Driscoll (1995) stated that waters with pH lower than 4.5 probably contain free mineral acids from volcanic gases or contamination from certain industrial wastes. Rainwater quality can be influenced by the pH level. A low pH level could induce the dissolution of trace and toxic elements into the rainwater.

2.2.2 CONDUCTIVITY (µS/cm)

Total dissolved solids (TDS) comprise inorganic salts (principally calcium, magnesium, potassium, sodium, bicarbonates, chlorides and sulphates) and some small amounts of organic matter that are dissolved in water (Hayes, 2004). Electrical conductivity (EC) is related to the amount of total dissolved salts (TDS), or the total amount of dissolved ions in water (Freeze and Cherry, 1979). Electrical conductivity is the ability of a substance to conduct an electrical current. The more salts are dissolved in water the higher is the value of the electrical conductivity. Pure water has a very low electrical conductivity because it contains only H_2O without salts or minerals. Conductivity changes with storage time and temperature. Measurement is therefore made in situ or in the field directly after sampling. Since each ion has its own specific ability to conduct current, EC is only an estimate of the total ion concentration. The water temperature affects the electrical conductivity so that its value increases from 2 up to 3% per 1 degree Celsius (Moore, 1989).The ability of rainwater to conduct an electrical current is it's conductivity. The electrical conductivity of rainwater is a function of temperature, type of ions present, and concentration of various ions. Conductivity readings are usually adjusted to 25^0C so that variations in conductivity are a function only of the concentration and types of dissolved constituents present (Freeze and Cherry, 1979). Thus in the absence of adequate data on total dissolved solids (i.e. all solid material in solution, whether ionised or not) electrical conductivity values could be used to express the total content of dissolved substances in the rainwater. The relationship between TDS (mg/L) and EC (μS/cm) is often described by a constant that varies according to chemical composition:

$$TDS = A \times EC \qquad (1)$$

Where;

A is in the range of 0.55 to 0.75

Typically the constant is high for chloride-rich waters and low for sulphate-rich waters. Chapman (1996). Freeze and Cherry (1979) and Davies and Dewiest (1996) classified waters into the following categories based on TDS; Freshwater (0-1000mg/L), Brackish water (1000-10000mg/L), Saline water (10000- 100000mg/L), Brine water (more than 100000mg/L). Low TDS values are normally associated with recharge areas and referred to as young waters while high TDS values are associated with discharge areas and referred to as old waters.

2.2.3 SALINITY

Salinity is the saltiness or dissolved salt content of a body of water. It is a general term used to describe the levels of different salts such as sodium chloride, magnesium and calcium sulfates and bicarbonates. Water can be classified as Fresh, Brackish, Saline and Brine depending on the salinity. Classification of water according to salinity is shown in table 1.

Table 1: Classification of water by Freeze and Cherry (1979).

Water Type	Salinity
Fresh water	< 0.5 ppt
Brackish water	0.5—30 ppt
Saline water	30---50 ppt
Brine	> 50 ppt

2.2.4 HARDNESS

Hardness is the ability of water to precipitate soap. Hard waters need considerable amounts of soap to produce lather and they produce scale in water pipes. Hard water is able to neutralize acid deposition in groundwater and reduce the solubility of toxic metals (Radojevic and Bashkin, 1999). The major contributors to water hardness are dissolved calcium and magnesium ions. These ions combine with soap to form insoluble precipitates.

2.2.5 ALKALINITY

Alkalinity is the capacity to neutralize acid. In water chemistry it is the capacity to accept protons (De Zuane, 1990). The primary sources of alkalinity in rainwater are carbonate ions (CO_3^{2-}), bicarbonate ions (HCO_3^-), and hydroxyl ions (OH^-); of these three, carbonate and bicarbonate are the most common. Total alkalinity is the sum of all three kinds of alkalinity.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \qquad (2)$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^- \text{…….pH } 4.5 \qquad (3)$$

$$H_2CO_3 \leftrightarrow 2H^+ + CO_3^{2-} \text{……. pH } 8.3 \qquad (4)$$

Measurements must be made in the field at the time of sampling since alkalinity is controlled by dissolution or degassing of CO_2 which can shift the source of alkalinity. The alkalinity value gives an estimate of non-acid constituents of water. When the “basic” constituents are limited to salts of calcium and magnesium, alkalinity equals hardness. When alkalinity is greater than hardness, basic salts, such as those of sodium and potassium, may also be present. When alkalinity is less than hardness, the presence of salts of calcium and magnesium are more likely to be sulphates instead of carbonates (De Zuane, 1990).

Radaideh et al., (2009) studied the quality of harvested rain water for domestic use. Their work focused on the quality of the rain water in different storage containers.

They concluded that rain water harvesting is an attractive option for increasing available water resources. However, the water in some of the storage containers were found to be heavily contaminated with microbes hence unsuitable for drinking. The study also found a significant variation in the quality of the stored water from different locations and recommended the following:

- Cleaning of rooftops or catchments before harvesting
- Locating cesspools far away from storage tanks
- Regular monitoring of the water quality
- Addition of disinfectants

Despins et al., (2009), studied rain water quality from rain water harvesting systems around the city of Guelph in Ontario, Canada. The study revealed about 31% and 13% of the samples were contaminated with total and faecal coliforms respectively. The study also observed a significant change in the quality of the rain water due to environmental conditions and a consistent high quality of the rain water through the selection of appropriate catchment and storage materials.

2.3 STABLE ISOTOPE STUDIES IN HYDROLOGY

Hydrological chemistry and stable isotopes in surface water have been used to examine the dynamics of river and lake mixing (Zhu et al., 2008; Yang et al., 2010, 2011), and to investigate groundwater recharge and evolution (Ma et al., 2005, 2009). Oxygen and hydrogen isotopes have also been used as a dating tool to identify the age of ground waters that are recharged under the colder-than-current climates of the late Pleistocene (Edmunds et al., 2006; Su et al., 2009)

In recent times, stable isotopes have contributed immensely to studies and investigations in hydrogeology. Many hydrogeological studies use the stable isotopes of water molecules to determine groundwater origin, recharge mechanism and rock water interaction (Fontes 1980).

Stable isotopes are those isotopes that do not undergo radioactive decay so their nuclei are stable and their mass numbers remain the same.

In hydrological studies, the stable isotope of most interest to hydrologist/ hydrogeologists are hydrogen and oxygen. Hydrogen has three isotopes of which two are stable; ^{1}H and ^{2}H and the unstable or radioactive ^{3}H. Oxygen also has three stable isotopes ^{16}O, ^{17}O and ^{18}O. The stable isotopes of oxygen-18 and deuterium are used in this study to provide information on hydrological processes. The relative abundance of these stable isotopes of hydrogen and oxygen are given in table 2.

Table 2: Relative Abundance of O and H Isotopes

Hydrogen		Oxygen	
Isotope	Abundance	Isotope	Abundance
^{1}H	0.99985	^{16}O	0.9975
^{2}H		^{17}O	0.00038
		^{18}O	0.00205

It is analytically difficulty to determine absolute isotope abundance but relative measurements based on the comparisms of the samples with a standard can be done easily and economically. For ^{18}O and ^{2}H the reference is Vienna Standard Mean Ocean Water (VSMOW) and results are expressed as parts per thousand (per mil, ‰), difference from the reference (Kendall and McDonnell, 1998).The isotopic ratios are expressed in delta units (δ) differences relative to an arbitrary standard.

$$\delta = (R/R_{STD} - 1)1000. \qquad (5)$$

Where, R and Rstd are the isotopes ratio of the samples and the standard respectively. The process by which the isotope content of water changes as a result of evaporation, condensation, freezing, melting, chemical reactions or biological processes is known as isotope fractionation (Fonte 1980). Evaporation of water results in isotope fractionation of hydrogen and oxygen such that ^{16}O and ^{1}H preferentially enter the vapour phase, while ^{18}O and ^{2}H are concentrated in the liquid phase (Freeze and Cherry, 1979).

Precipitation geochemistry results from an intricate series of interactions between cloud dynamics, microphysical processes and a series of rainout and washout chemical reactions in the atmosphere (Desboeufs et al., 2010). The combination of chemical data with stable isotope ($\delta^{18}O$ and $\delta^{2}H$) data in precipitation has proven to be a useful tool for exploring the relationship between the origins of air masses and the resulting precipitation characteristics (Craig, 1961; IAEA, 1980; Quereda et al., 1996; Ulrich et al.,1998; Balestrini et al., 2000; Celle-Jeanton et al., 2008; Prathibha et al., 2009); it has also been used to distinguish the different sources (i.e., natural inputs versus anthropogenic emissions) that contribute to rainwater chemistry (Tuncel and Ungor, 1996; Kulshrestha et al., 2003; Demirak et al., 2006; Yamanaka et al., 2007) and their potential impacts on eco-hydrosystems through deposition.

Several authors including; Harvey et al.,(2000) use stable oxygen and hydrogen isotopes to investigate the stable isotope composition of precipitation in the semi-arid north-central portion of US great plains, leading to the determination of the local meteoric water line for the site as $\delta^{2}H=7.66\delta^{18}O+4.96$. The oxygen and hydrogen stable isotope compositions of precipitation have also been used to investigate the origins of moisture in the Qilian Mountains (Zhou et al., 2007; Zhao et al., 2011), and the results indicated that regional precipitation is controlled by the Southeast Asian Monsoon in summer and by westerly and polar air masses in winter. Rainwater chemistry across the United States was studied by Root et al., (2004). Warrier et al., (2011), worked on isotopic composition of precipitation in wet tropic and semi-arid stations across southern India.

Understanding rainwater chemistry and its isotopic composition entails broad understanding of various parameters in relation to precipitation occurrences, movement and distribution in the prevailing hydrogeological cycle. This includes identification and characterization of hydrogeologic units, recharge-discharge conditions, aqueous geochemistry applications, and stable isotopes in hydrogeology.

2.4 HYDROGEOLOGICAL CYCLE

The continuous movement of water above, on, and below the surface of the Earth is called "hydrogeologic cycle" Figure 1. The cycle demonstrates three basic types of activity: inflows, outflows, and storage. An inflow is an increase in water to a part of the hydrologic cycle, while an outflow is a removal of water. The term "storage" refers to retention of water by a particular part of the system. If inflows to an aquifer exceed outflows, then the amount of water stored in the aquifer will increase, if outflows exceed inflows the amount of water held by the aquifer will decrease (Schlesinger, 1991). There are six major components to this cycle: evapotranspiration, condensation, precipitation, infiltration, percolation, and runoff.

Evapotranspiration refers to the combined effect of evaporation and transpiration. Evaporation is the process by which water is returned to the atmosphere; water on various surfaces (such as ponds, rivers, and oceans) is heated by the sun until it vaporizes and rises into the atmosphere. Transpiration refers to the return of moisture from parts of plants to the atmosphere.

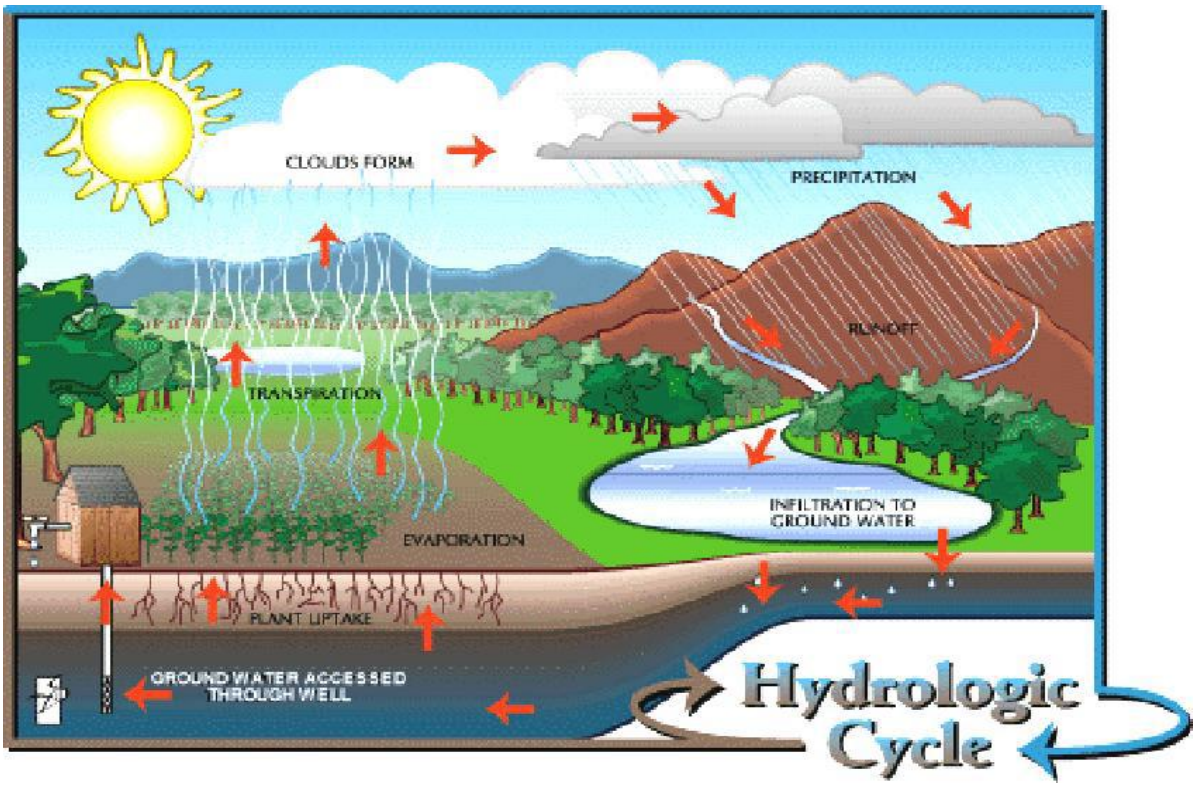

Figure 1: Hydrological Cycle Source US EPA (2000h)

As this moisture collects in the atmosphere, clouds form, eventually, the moisture falls as some form of precipitation such as rain.

The form, amount, and intensity of this precipitation vary by season and geographic location, and these variables determine whether or not water will flow into streams or infiltrate into the ground. As water begins to seep into the ground, it enters what is referred to as the unsaturated or vadose zone. This zone contains both water and air. The upper part of the zone, called the root or soil zone, supports plant growth and contains living roots, holes left by decayed roots, as well as animal and worm burrows (Hendrick and Flury, 2001). Beneath the root zone lays the intermediate zone, followed by the saturated capillary fringe. The saturated capillary fringe results from the attraction between water and rocks (Hendrick and Flury, 2001). This attraction causes water to cling as a film on the surface of rock particles. Water passes through the unsaturated zone to the saturated zone, where all the interconnected openings between rock particles are filled with water. It is within this saturated zone that we find “groundwater”. Infiltration also plays a role in maintaining the groundwater supply to wells, springs and streams. Physical characteristics of the soil, soil cover, water content of the soil, soil temperature and rainfall intensity all influence the rate of infiltration (Markus et al. 2004). The movement of water through soil and rock is referred to as “percolation”; the terms “infiltration” and “percolation” are frequently used interchangeably. The term “runoff” refers to the movement of water (typically from precipitation) across the earth’s surface to streams, lakes, oceans, and depressions in the surface; rainfall duration and intensity, slope of the ground, soil type, and ground cover may all influence the rate of such runoff (US EPA, 2000h).

2.5. RECHARGE-DISCHARGE CONDITIONS

Rainfall serve as one of the natural recharge of groundwater and it is an important part of the hydrologic cycle in which precipitation replenishes groundwater supplies.

The recharge rate is controlled by,

(i) the d-excess defined by the equation, ($\delta=\delta^{2}H-8\delta^{18}O$) is used to identify the origin and vapour source of rainfall (precipitation).

(ii) the saturation ratio of the atmosphere.

(iii) man’s activities such as emission of green house gasses and destruction of vegetation to impede transpiration, as the main factors that influence rainfall are transpiration and evaporation (Dunne et al.1991; Mcginty et al. 1979).

Rainwater is discharged in the form of precipitation. The intensity of precipitation varies by season and geographic location which in turn determines whether water will flow into surface waters or infiltrate into the ground. When discharge of rainwater is abstracted in the system, several adverse effects can occur. Most surface waters dry up and groundwater table level lowers resulting in springs and wells drying up. Rainwater should be considered as a non-renewable natural resource.

Chemical composition of water, as such rainwater determines the suitability as a source of water for consumption and other purposes. The quality of rainfall therefore reflects the inputs from the atmosphere, pollutant sources as in agriculture, mining, acid precipitation (rain), road users and industrial wastes (Appelo and Postma, 1993). Factors that influence rainwater quality in a particular area can be put as anthropogenic activities.

One of the most unusual characteristics of water is its ability to dissolve greater range of substances than any other liquid. The quality (chemical composition) of rainwater is it’s suitability as a source of water for human consumption and other purposes, and also influences ecosystem health function, (Appelo and Postma, 1993).

2.6 STABLE ISOTOPES STUDIES IN GHANA

In Ghana, several researchers had worked extensively on most surface and groundwater using isotopic studies; (Akiti, 1980 and 1986). Environmental isotope study of groundwater in crystalline rocks of the Accra Plains (Acheampong and Hess, 2000), origin of the shallow groundwater system in the Southern Voltaian sedimentary basin, Ghana.(Adomako et al., 2010a), geochemical and isotopic studies of groundwater conditions in the Densu River Basin of Ghana.(Adomako et al., 2010b), estimating groundwater recharge from water isotope ($\delta\ ^{2}H$, $\delta^{18}O$) depth profiles in the Densu River basin, Ghana.(Gibrilla et al., 2010b), origin of dissolved ions in ground waters in the northern Densu River Basin of Ghana using stable isotopes of ^{18}O and ^{2}H. (Akiti, 1980), worked so much in isotopic studies on both groundwater and rainwater from Aburi and Accra, south of Ghana to the north of Ghana leading to development of local meteoric water line for Ghana as, $\delta^{2}H= 7.86\delta^{18}O+13.62$.

In view of the studies that have been carried out on rainwater in Ghana, issues yet to addressed are

- There is little information on the combination of rainwater chemistry and stable isotopes in the Volta region
- The variation of rainwater chemistry in coastal, forest and mountainous areas in the Volta region
- The variation of rainwater stable isotopes in coastal, forest and mountainous areas of the Volta region
- The altitude effect on $\delta\ ^{18}O$ and $\delta\ ^{2}H$ in the lower parts of the Volta region
- Local Meteoric Water Line for the Lower Volta region.

CHAPTER THREE

3.0 MATERIALS AND METHODOLOGY

This chapter deals with the geography of the study area and the methods employed in analysing the various parameters in the rainwater.

3.1 THE STUDY AREA

The location consists of three main distinctive areas viz, coastal (Akatsi), mountainous (Amedzofe), and forest (Kpando) with four (4) administrative districts namely Akatsi District, Ho West District, Kpando District and Dayi District in Volta Region of Ghana. The Volta Lake stretches over and passes through two of the districts, precisely the forest area.

The coastal area lie between latitudes 02°57’10.2’’N to 02°64’20.8’’N of the equator and longitudes 06°73’05.7’’E to 06°77’17.4’E’ of the Greenwish Meridian with altitude range of about 29m to 56m above mean sea level. The altitude of the mountainous area ranges from 523m to737m above mean sea level, located in latitudes 06°51’09.9’’N to 06°49’32.0’’N of the equator and longitudes 00°26’06.3’’E to 00°25’33.4’’E of the Greenwish Meridian. The altitude of the forest area ranged from 112m to 244m above mean sea level, latitudes 07°00’22.7’’N to 06°55’21.1’’N of the equator and longitudes 00°17′05.9’’E to 00°20’23.9’’E of the Greenwish Meridian.

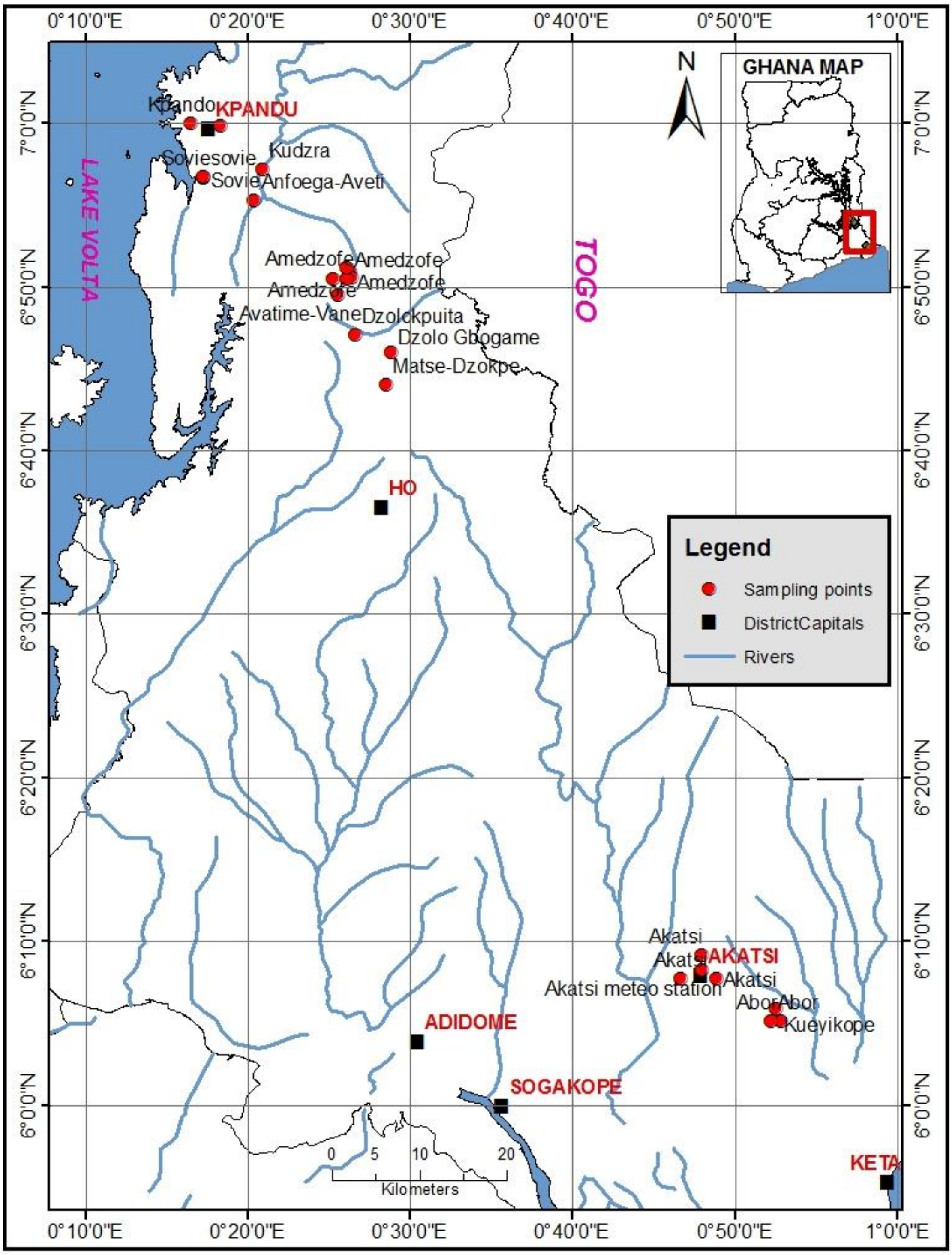

Figure 2: Map of the Study Area

3.2 VEGETATION AND CLIMATE

The vegetation is characterised by dense forest around Kpando, the forest area, moist semi-deciduous forest at Amedzofe, mountainous area and Akatsi the coastal area, is characterised by a mixture of open grassland and low bush.

The climate of the three areas is characterised by prevailing high temperatures marked with variations in the duration, high intensity and seasonal distribution of rainfall resulting in uniform moderately high temperatures throughout the year. The mean annual temperature of the three areas is about 27^{0}C, with February/March being the hottest (32 ^{0}C) and August being the coolest month (23 ^{0}C).

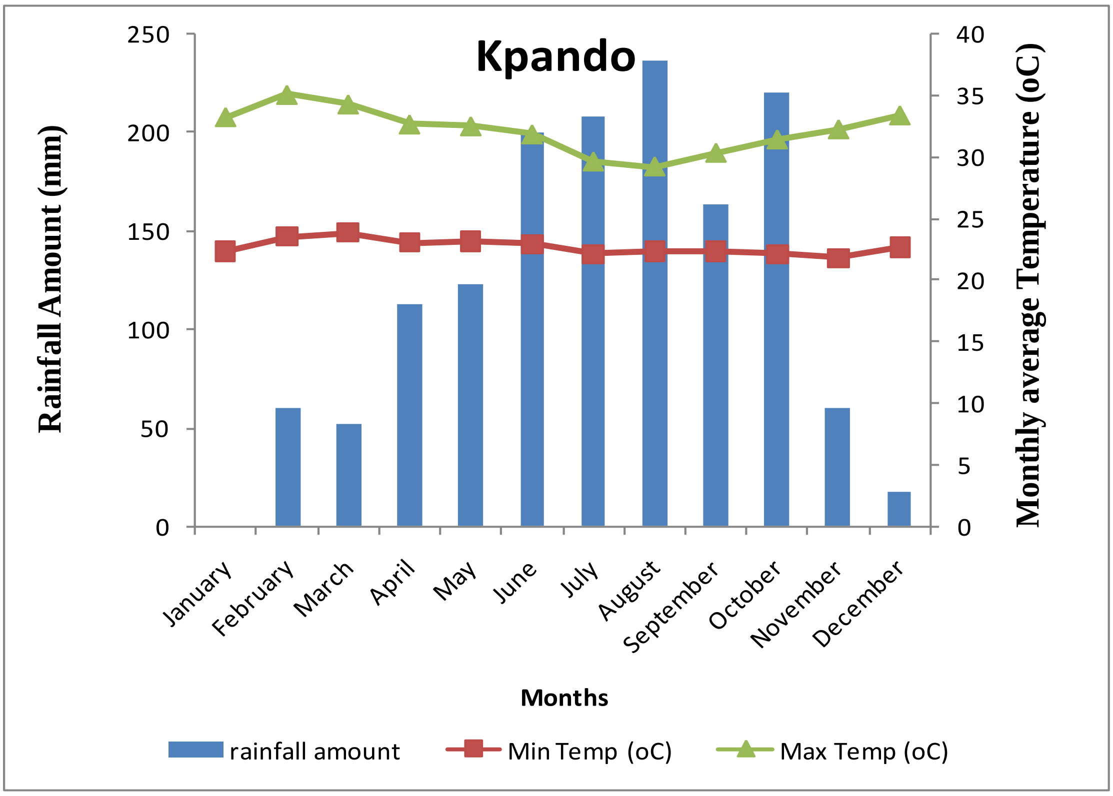

Figure 3: Monthly minimum and maximum temperature distributions and rainfall amount throughout the year in Kpando

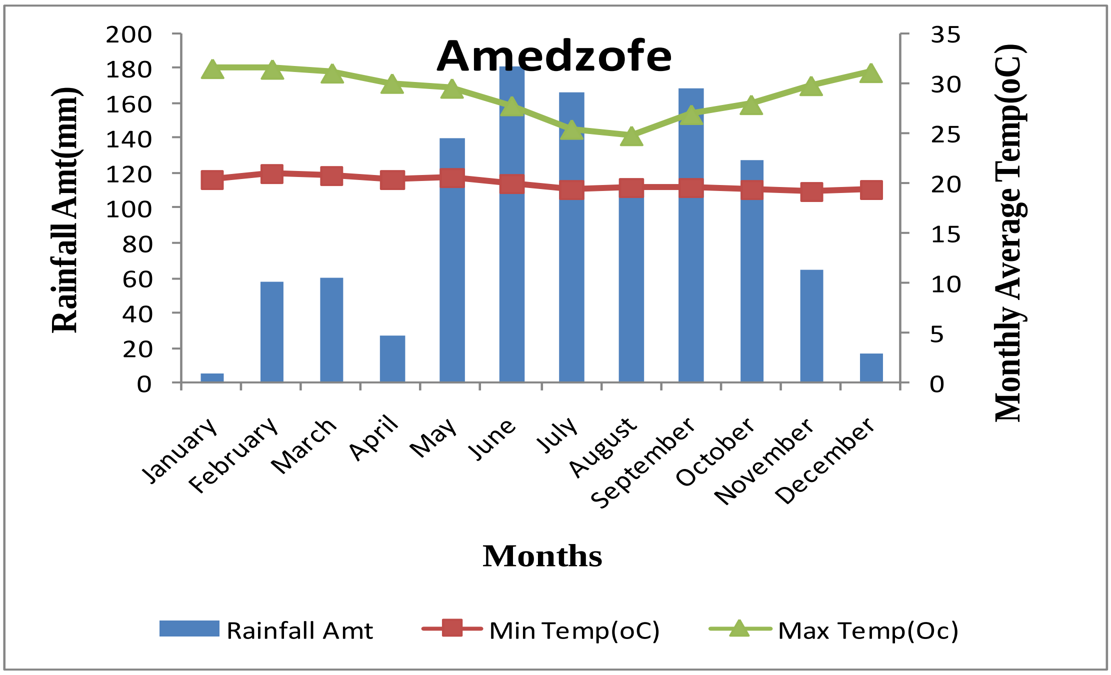

Figure 4: monthly minimum and maximum temperature distributions and rainfall amount throughout the year in Amedzofe.

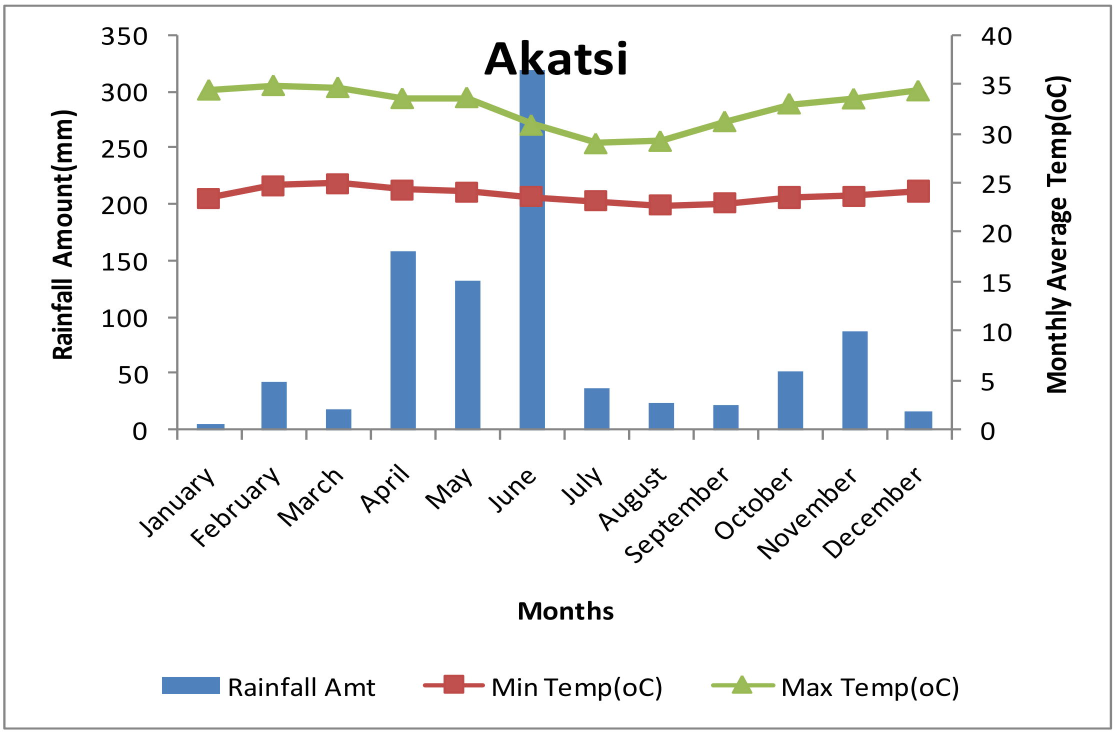

Figure 5: Monthly minimum and maximum temperature distributions and rainfall amount throughout the year in the Akatsi.

(Data source: Ghana Meteorological Agency. Accra)

The areas fall under two distinct climatic zones: the dry equatorial climate of the South East coastal plains, and the wet semi-equatorial climate further North from the coast. Both climatic zones are characterised by two rainfall periods with different intensities (Dickson & Benneh, 1998). The major rainy season extends from April/May to July and attains a peak in June which is seen in Akatsi and Amedzofe (Figures 4 and 5), when the maritime instability causes a surge of the moist south-westerly air stream resulting in the intensification of the monsoon rain.

The second rainfall period is a minor one that occurs between September and November, accompanied with several local thunder activities, especially in the forest and mountainous areas which are covered with moist semi-deciduous forest. This is then followed by the dry season. The annual rainfall ranges from 1700mm in the wet interior forest area through the mountainous to 800 mm in the dry equatorial zone near the coastal area.

3.3 DATA COLLECTION AND ANALYSIS

3.3.1 DESK STUDY

In order to achieve the set objectives, a desk study was carried out to assess the general hydrological and hydrochemical conditions prevailing in the study areas. It involved a review of literature, collection of topographical maps, collection of consistent five years rainfall and humidity data of the areas from Ghana Meteorological Agency, assessment of available equipments to carry out the analysis on the samples from Ghana Atomic Energy Commission-Chemistry department, Geological Survey Department and available literature from University of Ghana Library.

3.3.2 FIELD WORK

The procedure for fieldwork involved rainwater sampling from Akatsi(coastal), Amedzofe(mountainous), and Kpando (forest). Water sampling from few boreholes, hand-dug wells and springs and measurement of field parameters-pH, Electrical Conductivity (EC), Total dissolved solids (TDS), Salinity and Temperature (^{o}C) and HCO_3^- were involved. The sampling was carried out in a period of one year, from January 2013 to December 2013.

3.3.3. SAMPLE COLLECTION, ANALYSIS AND QUALITY ASSURANCE

One hundred and nine 330mL bottles of rainwater were sampled from Akatsi, Amedzofe and Kpando in a period of one year starting from January 2013 to December 2013, on an event basis, thus 23 rainfall events at Akatsi, 51 rainfall events at Amedzofe and 35 rainfall events at Kpando . A total of 21 groundwater samples were collected from the three areas comprising of 6 boreholes from Kpando, 6 boreholes from Akatsi and 6 boreholes, 3 springs from Amedzofe. The sampling points for the groundwater are shown in Figure 2.0. The groundwater samples were taken after evacuating several volumes of water using pumps installed in these wells. This was done to purge the aquifer of stagnant water and to acquire fresh aquifer samples for analysis. All the water samples were collected in 330mL high density polyethylene bottles. The bottles were conditioned by washing with five (5%) percent nitric acid, and then rinsed several times with distilled water. This was carried out to ensure that the sample bottles were free from contaminants. The samples were analysed for anions, cations, trace metals and isotopes. Rainwater and groundwater were collected directly in a preconditioned 60mL bottles with poly-sealed lids and tightly capped to prevent evaporation for stable isotopes of oxygen-18 and deuterium analysis.

Each sample bottle was provided with an identification labelled with the following information legibly and indelibly written:

- Sample identification number
- Date and time of sampling
- Record of any stability treatment
- Prevailing weather condition at the time of sampling

Only the groundwater samples were kept in an ice chest to maintain the temperature of the samples and then transported to the laboratory.

3.3.4 MEASUREMENT OF FIELD PARAMETERS

Temperature, electrical conductivity (EC) and total dissolved solids (TDS) measurements were conducted *in situ*, on the field by the HACH conductivity and pH metre. The pH meter was calibrated with standard pH buffers 4 and 7 and the conductivity meter calibrated with a 2191 μS/cm standard. The pH, EC, TDS, Temperature and salinity were then measured; about 100mL of water was placed in a beaker. Then the pH and conductivity meters placed simultaneously into the beaker of water and the readings taken when the meter stabilized.

Bicarbonate (HCO_3^-) concentration was done at the wellhead with a HACH field digital titrator by titrating 25mL aliquot of the sample with 0.02M hydrochloric acid

(HCl) cartridge using methyl orange as indicator. A change in colour, from orange to yellow indicates the endpoint and the volume of acid used recorded as titre value. The procedure was repeated three times and the average titre value calculated.

The reaction equation is as follows;

$$HCl(aq) + HCO_3^-(aq) \rightarrow CO_2(g) + H_2O(l) \qquad (6)$$

From the above equations, 1 mol of HCl reacts with 1 mol of HCO_3^- hence the concentration of HCO_3^- in millimol/L is calculated from the equation,

$$[HCO_3^-] = \frac{V_{T(HCl)}}{a} x \frac{M_{(HCl)}}{a} x1000 \qquad (7)$$

Where,

$V_{T(HCl)}$ = total volume of HCl needed for the titration

$M_{(HCl)}$ = Molarity of HCl

a = aliquot of sample in ml

The Molar Mass of HCO_3^- = 61

3.3.5 LABORATORY ANALYSIS

Various analytical methods have been employed in the determination of chemical composition of water (thus both rainwater and groundwater). This work involved the use of Flame Photometry, Atomic Absorption Spectrophotometry (AAS), UV Spectrophotometry, Ion Chromatography and Neutron activation analysis (NAA).

3.3.5.1 FLAME PHOTOMETRY

Sodium and potassium concentrations were determined using the flame emission photometer (Sherwood model 420). The photometer was calibrated as follows: 5mL of diluents was measured into a test tube and 2mL of 100ppm Li standard added. It was mixed well and aspirated. The blank knob was pressed. When channel 1 and channel 2 read 0.0 and 100.0 respectively 5mL of 100ppm Na/K standard was measured and 2mL of 100ppm Li standard was added. This was also aspirated and the set knob pressed from top to down so the reading on both channels read 100.0. After the calibration 5mL of each sample was measured and 2mL of 100ppm Li standard was added, mixed well and aspirated to measure both Na and K. The readings were read off the screen of the flame photometer and then recorded and where the readings exceeded the range, samples were diluted using de-ionized water and measured.

3.3.5.2 ION CHROMATOGRAPHY

The anions (Cl^-, NO_3^-, SO_4^{2-}) were analysed using the Dionex ICS-90 ion chromatograph system at the laboratory of the National Nuclear Research Institute, NNRI, of the Ghana Atomic Energy Commission .The Dionex ICS-90 ion chromatograph system performs isocratic ion analysis. An ICS-90 typically consists of a liquid eluent, a high pressure pump, a sample injector, a separator column, a chemical suppressor and a conductivity cell. Before the samples were analysed, the ICS-90 was calibrated using a standard anion solution (seven anion standard II).The samples were filtered with a 0.45µm size pore filter paper. Samples with salinity above 0.1ppm were diluted. Each sample mixes with nitrogen gas and the eluent in the injection valve. The mixture then passes through the column guard and gets to the analytical column which is made up of resins. Here the anions are separated based on their weight with each retention time; (that is Cl^-, NO_3^-, SO_4^{2-}).

The standards were read first. With each retention time, a calibration curve was drawn with the peak height or area. The sample peak was then extrapolated in the calibration curve to get the concentration. A detector detects the anions and interprets their concentrations in the form of peaks. A computer running chromatograph software automatically converts each peak in a chromatograph to a sample concentration and produces a tabulated print of the results.

3.3.5.3 ATOMIC ABSORPTION SPECTROMETRY

Samples were analysed for Mg^{2+} at NNRI laboratory GAEC, using a Varian AA240 Fast Sequential Atomic Absorption Spectrometer Samples were previously acid digested using HCl, HNO_3 and H_2O_2.

3.3.5.4 INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

For Instrumental neutron activation analysis, trace elements were analyzed in water samples at GHARR-1, GAEC.

The PC–based gamma ray spectroscopy system was used for the measurement. The spectroscopic system consists of an n-type HPGe detector model GR 2518 and HV power supply model 3103, a spectroscopy amplifier model 2020 and 74 ACCUSPEC Multichannel Analyser (MCA) emulation software (all manufactured by Canberra Industries Inc.). The relative efficiency of the detector is 25%.

0.50ml of 12 water samples, comprising of 2 rainwater, 2 groundwater from Akatsi; 2 rainwater, 2 groundwater from Kpando and 2 rainwater, 2 groundwater from Amedzofe (weighing 0.50gram) were pipette using a calibrated Eppendorf tip ejector pipette (Brinkmann Ins., Inc., Westbury, NY) into clean pre-weighed 1.5mL polyethylene vials, and fitted with polyethylene snap caps and heat-sealed. Four of these samples vials were placed into a 7.0mL volume polyethylene vial and heat-sealed for medium lived radionuclide for irradiations. Two replicates were prepared for each sample. However, for short lived radionuclide, only one sample was put into the 7.0ml vial.

The samples were irradiated using the GHARR-1 reactor operating at half full power of 15kW and at a neutron flux of 5.0×10^{11} neutrons/cm^{2}s. The scheme for irradiation was chosen according to the half lives of the elements of interest. For the short-lived elements with half-lives up to 20min, irradiation time of 120sec was chosen. For medium –lived elements, that is, those with half-lives between 20min and 3days, the irradiation times were limited to 10-60min. The water samples and the elemental comparator standards were sent into the reactor by means of a pneumatic transfer system operating at a pressure of 1.723 bars. At the end of the irradiation, the capsules were returned from the reactor and allowed to cool down until the level of activity was within the 2.5-10% of the dead time of the detector. The samples were placed on the detector at counting geometry of 7 and counts were accumulated for a preselected time to obtain the spectra intensities. For short and medium irradiations, 600sec counting time was chosen.

3.3.5.4.1 EXPECTED TRACE METALS NORMALLY FOUND IN WATER SAMPLES

Table 3: Nuclear data of elements determined in this work

Elements	Target Isotope	Formed Isotope	Half life	Gamma ray Energy Kev
Cu	^{65}Cu	^{66}Cu	5.10min	1039.2
Al	^{27}Al	^{28}Al	2.24min	1778.9
V	^{51}V	^{52}V	3.75min	1434
Mn	^{55}Mn	^{56}Mn	2.58h	2113
Hg	^{196}Hg	^{197}Hg	64.1h	77.4
Cd	^{114}Cd	^{115}Cd	53.46h	527.9
As	^{75}As	^{76}As	26.32h	559.1

3.3.5.4.2 NEUTRON-GAMMA REACTION FOR THE TRACE ELEMENTS/METALS

The targets elements will undergo neutron-gamma reaction where by thermal neutrons will interact with target nucleus in radiative capture reaction to produce isotopes.

That is;

$$^{27}\mathrm{Al}(n, \gamma)^{28}\mathrm{Al} \tag{8}$$

$$^{114}\mathrm{Cd}(n, \gamma)^{115}\mathrm{Cd} \tag{9}$$

$$^{75}\mathrm{As}(n, \gamma)^{76}\mathrm{As} \tag{10}$$

$$^{65}\mathrm{Cu}(n, \gamma)^{66}\mathrm{Cu} \tag{11}$$

$$^{51}\mathrm{V}(n, \gamma)^{52}\mathrm{V} \tag{12}$$

$$^{55}\mathrm{Mn}(n, \gamma)^{56}\mathrm{Mn} \tag{13}$$

$$^{201}\mathrm{Hg}(n,\gamma)^{202}\mathrm{Hg} \tag{14}$$

3.3.6 STABLE ISOTOPE ANALYSIS

All samples were analysed for oxygen-18 and deuterium in the Isotope Hydrology Laboratory of the Nuclear Chemistry and Environmental Research Centre, Ghana Atomic Energy Commission. The samples were analysed using the off-axis integrated cavity output spectroscopy (OA-ICOS) Los Gatos Research DT-100 Liquid-Water Isotope Analyser (Model 908-008-2000).

This equipment also called the Liquid Water Isotope Analyser (LWIA) measures absorption around a wavelength of 1390 nm to calculate molecular concentrations of ^{2}HHO, HH^{18}O and HHO. Molecular concentrations are converted into atomic ratios, $^{2}H/^{1}H$ and $^{18}O/^{16}O$ and a post-processing procedure was used to calculate delta-scale (δ) values with respect to Vienna Standard Mean Ocean Water (VSMOW) (Coplen, 1996) as stated in equation 5.

The instrument contains the laser analysis system and an internal computer, a 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. The autosampler and the DLT-100 are connected by a ~1 m long polytetrafluoroethylene(PTFE) transfer line. A Hamilton microlitre syringe (model 7701.2N) was used to inject 0.75 litre of sample through a PTFE septum in the autosampler. The injection port of the autosampler was heated to 80°C to help vaporize the sample under vacuum immediately upon injection. The vapor then travels down the transfer line into the pre-evacuated mirrored chamber for analysis. The instrument has a precision of approximately 1‰ for δ^2H and 0.2‰ for δ^{18}O.

To improve the quality of the results, randomly selected samples and some of the external standards were also re-analysed as controls. All samples were analysed in duplicate. Large standard deviations from re-analysed samples or duplicates were evidence of poor analysis. Acceptable values were within 0.01–0.05‰ vs. V-SMOW for ^{18}O and 0.1–0.5‰ vs. V-SMOW for ^{2}H.

CHAPTER FOUR

4.0 RESULT AND DISCUSSION

This chapter deals with the general interpretation of the rainwater parameters such as temperature, pH, electrical conductivity, major ions such as Na^+, Mg^{2+}, HCO_3^-, Cl^-, K^+, Ca^{2+}, SO_4^{2-}, and NO_3^- which will be discussed under hydrochemistry of rainwater. Trace metals in the rainwater will also be discussed and the last section will deal with the groundwater chemistry and the isotope data.

4.1 HYDROCHEMISTRY OF RAINWATER IN THE STUDY AREA

The quality of the rainwater at Akatsi, Amedzofe and Kpando was determined by analyzing the physico-chemical parameters. Table 4, shows the result of the physical and chemical parameters in the study area and Figure 6 indicates the variation of physical parameters.

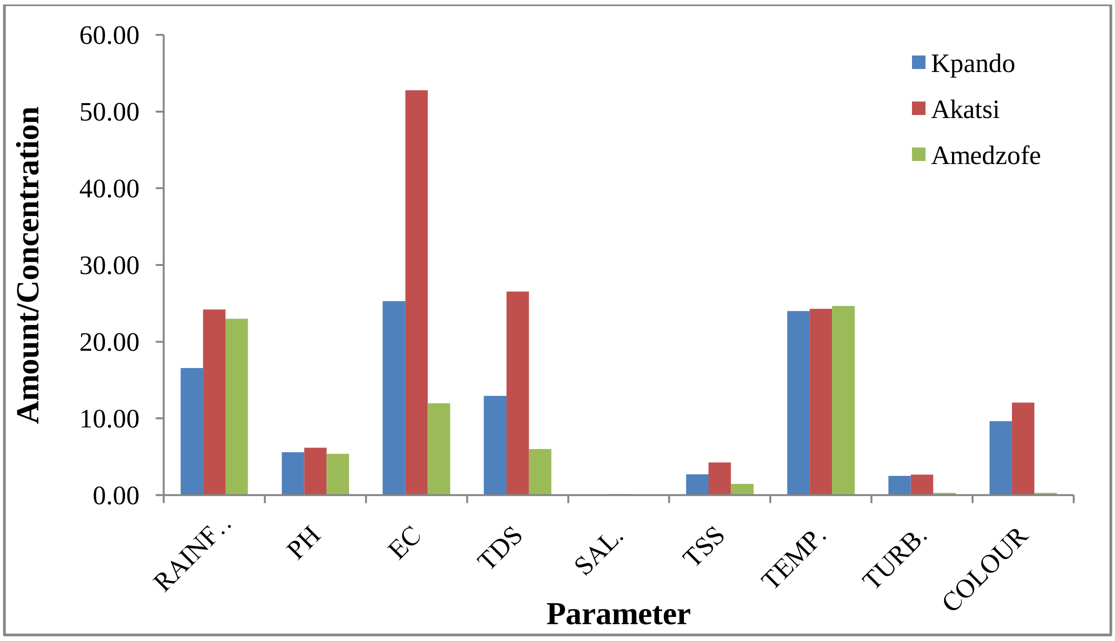

Figure 6: Variation of physical parameters

Table 4: Statistical summary of the physico-chemical parameters from the study areas.

		Kpando			Akatsi			Amedzofe		
Parameter	Units	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
RAINFALL	mm	2.20	71.80	16.55	3.40	83.00	24.21	4.20	72.00	22.98
pH	pH units	4.79	6.00	5.60	5.40	6.85	6.19	4.30	6.30	5.38
EC	us/cm	7.98	92.20	25.27	8.74	173.60	52.78	2.43	50.30	11.98
TDS	mg/L	4.30	46.80	12.94	4.80	86.83	26.55	1.20	25.20	5.99
SAL.	ppt	0.00	0.10	0.00	0.00	0.70	0.13	0.00	0.10	0.00
TSS	mg/L	0.00	9.00	2.71	0.00	24.00	4.26	0.00	5.00	1.45
TEMP.	°C	23.70	24.20	24.00	23.80	25.00	24.28	23.80	25.00	24.67
TURB.	NTU	0.00	9.00	2.51	0.00	16.00	2.65	0.00	3.00	0.29
COLOUR	Pt/Co	0.00	24.00	9.66	0.00	67.00	12.04	0.00	10.00	0.31
Na^+	mg/L	1.40	24.50	4.46	2.30	17.50	6.75	0.00	5.60	0.88
K^+	mg/L	0.00	5.30	1.24	0.30	13.60	3.86	0.00	2.60	0.25
Ca^{2+}	mg/L	0.64	5.12	2.31	0.64	19.84	3.13	0.80	3.52	1.87
Cl^-	mg/L	7.99	20.49	14.31	15.49	95.97	28.51	1.19	17.99	7.98
OH^-	mg/L	8.00	40.00	18.74	10.00	104.00	34.52	8.00	24.00	12.59
HCO_3	mg/L	9.75	48.76	22.85	12.19	126.79	42.06	9.75	29.26	15.35
SO_4^{2-}	mg/L	1.17	73.20	17.44	10.68	73.10	38.69	-3.98	21.36	6.11
NO_3^-	mg/L	0.05	0.61	0.29	0.01	0.89	0.29	0.00	0.74	0.23
Mg^{2+}	mg/L	0.09	1.54	0.75	0.00	1.16	0.65	0.00	0.98	0.21

4.1.1 pH

The pH values of individual rainfall ranged from 5.40 to 6.85 at Akatsi (coastal). The mean value of the pH is 6.19, of which 26.1% of the rainfall event had pH range of 5.0 to 6.0. No event recorded pH in the range of 4.0 to 5.0. Majority of the rainfall events, about 73.9% fell in the range of 6.0 to 7.0 pH. This indicates that the rainwater samples from Akatsi are slightly acidic to neutral and this could result from industrial activities and vehicular emissions. The values are within the WHO standards (6.50 to 8.50).

Amedzofe (mountainous) samples had the mean pH value of all the individual rainfall to be 5.38, of which 13.70% of the rainfall event had pH ranging from 4 to 5. 82.40% of the rainfall event fall within pH of 5 to 6 and 3.90% had pH range of 6 to 7. About 96.10% of the total rainfall event had pH less than 6. These low pH values consequently reflect a significant impact of anthropogenic activities on rainwater quality in the study area. This may be due to carbon monoxide and carbon dioxide produced from bush burning in the area.

On the other hand, the pH values of the individual rainfall ranges from 4.76 to 6.00 at Kpando (forest) with a mean value of 5.60. Of the entire rainfall event at Kpando, 2.9% had pH ranges between 4.0 to 5.0, and 6.0 to 7.0, while 94.2% had pH range of 5.0 to 6.0. From the data, it could be deduced that majority, over 90% of the rainfall events had pH less than 6.0 which is the pH value of unpolluted water at equilibrium with atmospheric CO_2 (Seinfeld, 1986; Charlson and Rodhe,1982).

Low pH values can be attributed to wet atmospheric deposition of CO_2, SO_2 and NO_2 produced by vehicular emissions and the ‘‘cut and burn’’ method of land preparation for farming in the study communities. Kohler et al. (1997) in their study of the contribution of aircraft emission to atmospheric nitrogen content states that rainwater acquires slight acidity as it dissolves CO_2 and NO_2 gases in the atmosphere.

In all the three stations, Amedzofe recorded the lowest mean pH, and this could be due to the movement of air masses.

4.1.2 ELECTRICAL CONDUCTIVITY

From the results presented, conductivity values of all the rainfall events from the three areas were lower than the standard value presented by WHO as 1000 µS/cm. Thus at Akatsi a range of 8.7 to 173.6µS/cm was recorded with a mean value of 52.8 µS/cm. Range of 2.4 to 50.3µS/cm was recorded at Amedzofe with a mean of 12.0 µS/cm and a range of 8.0 to 92.2 µS/cm was recorded at Kpando with a mean of 25.3 µS/cm. The results indicate the low electrical current conductivity of water. EC is affected by the presence of inorganic dissolved solids such as chloride, nitrate, and sulphate anions (ions that carry negative charge) or sodium, magnesium, and calcium cations [ions carrying positive charges] (Igwo-Ezikpe et al.,2010) .

Moreover, the total dissolved solids values are also generally low as compared to the WHO values obtained. Subramanian, (2004) observed that rainwater contain low minerals and has very little dissolved substances.

The low mean values of turbidity 2.65NTU recorded at Akatsi, 0.29 NTU at Amedzofe and 2.51NTU at Kpando, indicate the absence of suspended particles or if any, little. This is probably due to low levels of particulates such as smoke, dust, and soot suspended in the atmosphere which dissolved in the rain droplets as it fell from the cloud. This may also be related to the presence of particles of clay, organic components and other microscopic substances (Ovrawah and Hymone, 2001). In addition, the low turbidity in the rainwater can be associated with frequent rainfalls during the sampling period. Appiah (2008) in the study of physicochemical analysis of roof run-off observed that turbidity is affected by dry spell, and the longer the span of continuous rainfalls, the lower is the turbidity. Hence there will be no problems during purification, no possibility of micro-biological contamination, no low dissolved oxygen, and no decrease in the rate of photosynthesis in the study area.

4.1.3 TEMPERATURE

The temperature of the study area ranges from 23.8^oC to 25.0^oC at Akatsi (coastal), with the mean temperature of 24.3^oC. Temperature range of 22.8^oC to 24.9^oC, and a mean of 24.5^oC were recorded at Amedzofe (mountainous) and temperature, ranging from 23.7^oC to 24.2^oC was recorded at Kpando (forest) with the mean value of 24.0^oC. Temperature has great impact on the microbiological quality of rainwater, and from the temperature values obtained, there was not much variation in the study area, as such temperature would not have much effect on other parameters.

4.1.4 COLOUR

The colour levels of rainwater recorded ranged from 0.0 to 67 Hz with a mean value of 12.04 Hz at Akatsi, 0.0 to 10.0 Hz with a mean of 0.31 Hz at Amedzofe and .0 to 24.0 Hz with a mean of 9.66 Hz at Kpando, compared with WHO guidelines of 15 Hz for drinking water. Colour is strongly influenced by the presence of iron and other metals, either as natural impurities or as corrosion products.

4.2 MAJOR IONS

The concentration of major ionic species in the rainfall sampled at the three zones in the study areas had the following order; HCO3->SO42->OH->Cl-$>Na^{+}>K^{+}>Ca^{2+}>Mg^{2+}>NO_3^{-}$, for Akatsi (coastal); $HCO_3^{-}>OH^{-}>Cl^{-}>SO_4^{2-}>Ca^{2+}>Na^{+}>K^{+}>NO_3^{-}>Mg^{2+}$, for Amedzofe (mountainous) and $HCO_3^{-}>OH^{-}>SO_4^{2-}>Cl^{-}>Na^{+}>Ca^{2+}>K^{+}>Mg^{2+}>NO_3^{-}$,for Kpando (forest);. The alkaline components namely, Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} contribute about 9.10% of the total ionic strength for Akatsi rainfall; 7.10% for Amedzofe rainfall and 10.62% for Kpando rainfall, whereas the acidic components comprising of SO_4^{2-},Cl^{-},HCO_3^{-} and NO_3^{-} made up 90.90% for Akatsi rainfall, 92.90% for Amedzofe rainfall and 89.38% for Kpando rainfall.

4.2.1 NITRATE

Nitrates and nitrites are naturally occurring ions that are left after breakdown or decomposition of animal or human waste, Camilli, L. (2000). The data obtained from the three areas show very low level of this ion as 0.29mg/L, 0.23mg/L and 0.29mg/L, for Akatsi, Amedzofe and Kpando respectively. This means that, the occurrence of methaemoglobinaemia (blue-baby syndrome, thus showing lack of movement of oxygen in organic tissues) may not be experienced in the study area. However, low levels of the element in the human system may result in the inability to break down methaemoglobin rapidly with associated health implication.

The presence of nitrates in the rainwater samples may be due to direct dissolution and oxidation of NO_2 to NO_3^{-} resulting from the use of nitrogen fertilizers for crop cultivation in the study area. This observation is buttressed by Thomas and Grenne, (1993) in their study of rainwater quality from different roof catchments in agricultural areas, rainwater could have higher concentration of nitrate due to fertilizer residue in the atmosphere. As observed during the survey, residence at the study areas are engaged in farming, this might have introduced nitrates in the rainwater.

4.2.2 SULPHATE

The levels of sulphates were also found to be lower than the recommended WHO standard (200mg/L). In Akatsi the sulphate in rainfall ranged from 10.68mg/L to 73.10mg/L with a mean value of 38.69mg/L. Amedzofe ranged from -3.98mg/L to 21.36mg/L with a mean of 6.11mg/L, whilst Kpando had a minimum sulphate value of 1.17mg/L and maximum value of 73.20mg/L with a mean of 17.44mg/L.

Sulphate contributes to the sour taste and strong ‘rotten-egg’ odour and contributes to corrosion of metal pipes in delivery systems. It can therefore be said that, the water will not taste sour and will have a pleasant smell because the values recorded from the three areas were lower than the guidelines value, even though Akatsi seems to be the highest among the areas, which could be attributed to the fact that it is situated closer to a heavy industrial area of Ghana, (Tema) hence wind trajectory might had brought about the high value.

Generally, it is established that sulphate is formed in the atmosphere by chemical conversion from SO_2, which is discharged into the atmosphere from natural and anthropogenic sources. SO_2 is gradually converted to aerosols by oxidation as it is carried by moisture laden air currents downwind from its sources. However, the study recorded low sulphate concentrations that suggest that SO_2 discharged into the atmosphere from human activities in the study area could be moderate or insignificant.

4.2.3 CHLORIDE

Chloride concentration of rainfall in Akatsi ranged from 15.49 to 95.97mg/L with a mean of 28.51mg/L, compared to WHO limit of 250 mg/L for portable water. Amedzofe rainfall chloride concentration ranged from 1.19 to 17.99mg/L with a mean value of 7.98mg/L. Kpando rainfall ranged from 7.99 to 20.49mg/L with a mean value of 14.31mg/L. The main source of Chloride in rain is sea aerosol spray. However human activities and industrial activities can produce HCl in gas phase which could dissolve in the rain (Younos et al., 1998). The low chloride concentration of the rainfall recorded during the study period might also be attributed to the low industrial emissions in the study area.

4.2.4 ALKALINITY AND BICARBONATE

The total alkalinity of the rainfall at Akatsi during the study ranged from 10 to 104 mg/L with a mean value of 34.52 mg/L compared with WHO limit of 1000 mg/l for drinking water. Amedzofe rainfall ranged from 8 to 24 mg/L with a mean value of 12.59 mg/L and Kpando from 8 to 40 mg/L with a mean of 18.74 mg/L. These are very low concentrations.

The bicarbonate concentration of the rainfall ranged from 12.19 to 126.79 mg/L with a mean of 42.06 mg/L at Akatsi. Amedzofe ranged from 9.75 to 29.26 mg/L with a mean of 15.35 mg/L and 9.75 to 48.76 mg/L with a mean of 22.85 mg/L at Kpando. Water can dissolve carbon dioxide from the air, forming carbonic acid (H_2CO_3). The concentration is as a result of the high presence of CO_2 in the atmosphere due to bush burning in the study area and its environs.

4.2.5 SODIUM

Sodium concentration in Akatsi rainfall ranged from 2.3 to 17.5mg/L with a mean of 6.75mg/L, Amedzofe ranged from 0 to 5.6mg/L with a mean of 0.88mg/L and Kpando rainfall ranged from 1.4 to 11.3 mg/L with a mean of 3.89 mg/L. The values are far lower than the standard for drinking water. Sodium is generally taken as the best reference element for marine sources. Nevertheless, it is reported that for individuals suffering from health problems such as heart disease or high blood pressure the maximum recommended sodium concentration in drinking water is 20 mg/L (Younos et al., 1998).This implies that rainwater from the study area will not pose any health problem to such people.

4.2.6 POTASSIUM

The potassium concentration ranged from 0.3mg/L to 13.6mg/L with a mean value of 3.86mg/L in Akatsi rainfall, Amedzofe ranged from 0.0mg/L to 2.6mg/L with a mean concentration of 0.25mg and 0.0 to 5.3mg/L potassium concentration with a mean of 1.24mg/L was recorded at Kpando. Comparing these values to WHO limit of 30 mg/L for drinking water it could be deduced that potassium concentration in rainfall from the study area is very low. K^+ has been suggested as a chemical signature of biomass burning (Khare, et al., 2004). This therefore revealed that the ongoing annual bush burning activity in the study area contributes to potassium concentration in the rainwater. So from the values obtained, it could be said that there was not much such activity in the study area.

4.2.7 CALCIUM AND MAGNESIUM

Calcium concentration ranged from 0.64mg/L to 19.84mg/L with a mean of 3.13mg/L at Akatsi, Amedzofe ranged from 0.80mg/L to 3.52mg/L with a mean of 1.87mg/L and 0.64mg/L to 5.12mg/L at Kpando with a mean value of 2.31mg/L.

The Magnesium concentration of the rainwater ranged from 0.00 to 1.16mg/L with a mean of 0.65mg/L at Akatsi, 0.00 to 0.09mg/L with a mean value of 0.21mg/L at Amedzofe and 0.09 to 1.54mg/L with a mean of 0.75mg/L at Kpando.

However, the low concentrations of these minerals in rainwater have the tendency of causing health problems since water scarcity is compelling large number of the populace in the study area to patronize rainwater highly. Soft water (that is water low in calcium and magnesium), is associated with increased morbidity and mortality from cardiovascular diseases (CVDs) compared to hard water and water high in magnesium (Donato et al., 2003). Recent studies also suggest that the intake of soft water may be associated with high risk of fracture in children, (Verd et al., 1992). A few months exposure may be sufficient consumption time effects from water that is low in magnesium and/or calcium.

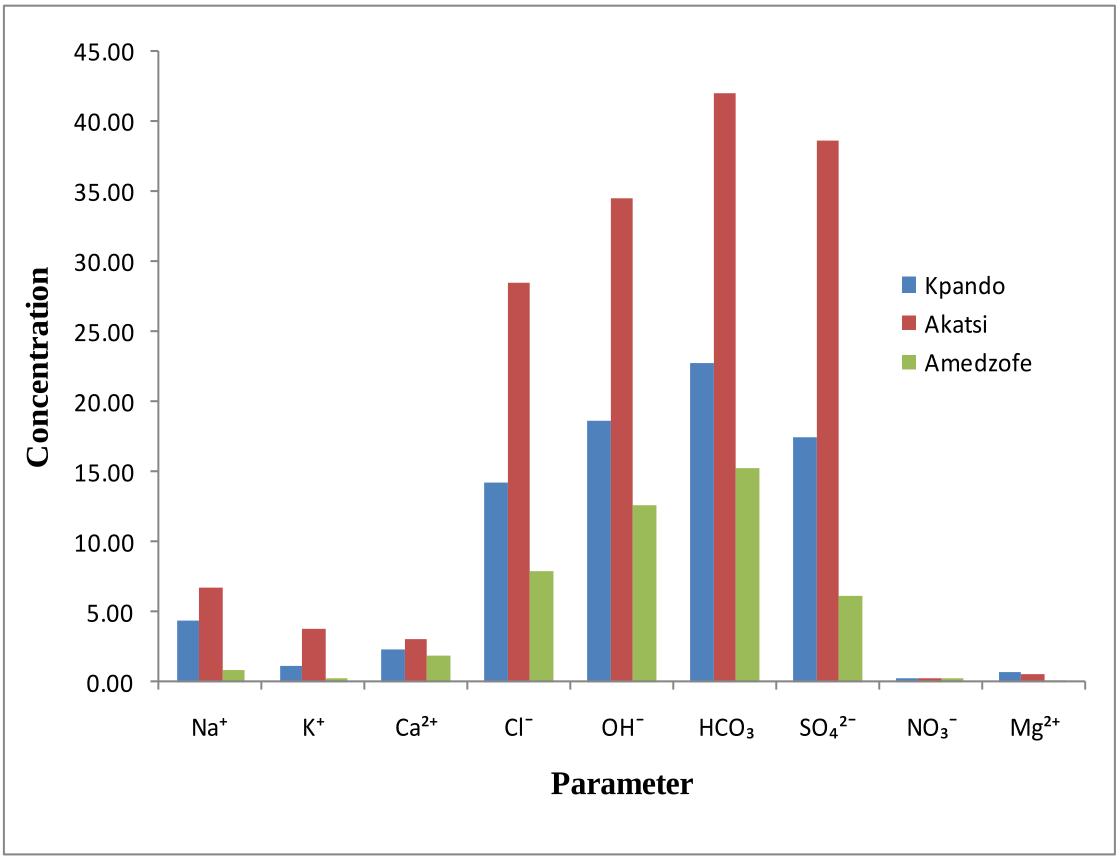

Figure 7: Variation of chemical parameters of rainwater.

4.2.8 CATION ORDER OF DOMINANCE IN THE STUDY AREA

- Akatsi; $Na^{+} > K^{+} > Mg^{2+} > Ca^{2+}$
- Amedzofe; $Ca^{2+} > Na^{+} > K^{+} > Mg^{2+}$
- Kpando; $Na^{+} > Ca^{2+} > K^{+} > Mg^{2+}$

4.2.9 ANION ORDER OF DOMINANCE IN THE STUDY AREA

- Akatsi; $HCO_3^- > SO_4^{2-} > OH^- > Cl^- > NO_3^-$
- Amedzofe; $HCO_3^- > OH^- > Cl^- > SO_4^{2-} > NO_3^-$
- Kpando; $HCO_3^- > OH^- > SO_4^{2-} > Cl^- > NO_3^-$

4.3 TRACE ELEMENTS ANALYSIS IN THE RAINWATER

Table 5: Summary of trace elements analyzed

Trace Elements	Min	Max
Cu	<0.001	7.92
V	<0.01	0.43
Mn	0.26	1.43
Cd	<0.01	<0.01
Hg	<0.01	<0.01
As	<0.001	<0.001
Al	0.18	0.93

4.3.1 COPPER, MANGANESE, VANADIUM AND ALUMINIUM

These four trace metals are short-lived radionuclides with irradiation time of 10minutes.

The concentration of Copper ranges from below the detection limit of 0.001 to 7.92 ± 1.12 mg/L. The concentration of Manganese ranges from 0.26 ± 0.04 to 1.43 ± 0.21 mg/L. The concentration of Vanadium within the entire study area ranged from below the detection limit of 0.01 to 0.43±0.06 mg /L. Aluminium concentration of the entire samples ranged from 0.18±0.25 to 0.93±0.16 mg/L. The permissible limit of these metals in water by WHO are; Cu 2.0 mg/L, Mn 0.4 mg/L, V 0.2 mg/L and Al 0.03 mg/L. It could be seen that some rainwater samples have concentrations of these metals beyond the limit especially rainwater samples from Amedzofe, which could be due to movement of wind direction from the coast.

4.3.2 CADMIUM, ARSENIC, AND MERCURY

The concentration of cadmium in the rainwater fell below the detection limit of 0.01mg/L. Arsenic concentration in the entire samples was below the detection limit of 0.001mg/L. Mercury concentration in the rainwater samples is below detection limit of 0.01mg/L. These are medium- lived radionuclides with irradiation time of 60 minutes.The recommended level of these metals are: Cd 0.003mg/L, As 0.01mg/L and Hg 0.001mg/L. The values obtained for these metals are far below the recommendation, so they will not pose any health problem.

4.4 STABLE ISOTOPES VARIATION OF RAINFALL IN THE THREE STATIONS

The statistical summary of the stable isotope and the rainfall amount for the study period at the three locations are given in Table 6 while the detailed results are presented in appendix B.

The $\delta^{18}O$ values for Akatsi, Amedzofe and Kpando ranged from -5.57to +0.26 ‰ vs VSMOW, -6.54 to +2.73 ‰ vs VSMOW, -5.52 to +2.39 ‰ vs VSMOW and with respective mean values of -1.82 ‰ vs VSMOW, -2.93 ‰ vs VSMOW, -2.07 ‰ vs VSMOW.

The δ^2H values also, ranged from -30.16 to +7.12 ‰ vs VSMOW for Akatsi, -41.38 to +14.72 ‰ vs VSMOW for Amedzofe, and -29.57 to +22.99 ‰ vs VSMOW for Kpando with mean values of -6.55 ‰ vs VSMOW, -14.12 ‰ vs VSMOW and -6.44 ‰ vs VSMOW respectively. Stable isotope content of precipitation at the three stations showed significant variations with the mean $\delta^{18}O$ value of Akatsi (coastal) being enriched. The isotopic composition of local precipitation is primarily controlled by regional scale processes like the trajectories of the water vapour transport over the continent and the average rainout history of the air masses giving precipitation at a particular place (Rozanski et al., 1982)

Table 6: Statistical summary of rainfall, $\delta^{18}O$ and δ^2H at the three stations

	Amedzofe			Kpando			Akatsi		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Rainfall	4.20	72.00	22.98	2.20	71.80	16.55	3.40	83.00	24.21
$\delta^{18}O$	-6.54	+2.73	-2.93	-5.52	+2.39	-2.07	-5.57	+0.26	-1.82
δ^2H	-41.38	+14.72	-14.12	-29.57	+22.99	-6.44	-30.16	+7.12	-6.55

Rainfall in mm,

The plot $\delta^{18}O$ and δ^2H of Akatsi, Amedzofe and Kpando together with Global Meteoric Water Line (GMWL) define by $\delta^2H = 8\ \delta^{18}O + 10$ and Local Meteoric Water Line (LMWL) defined by $\delta^2H = 7.86\ \delta^{18}O + 13.61$ (Akiti et al.,1980) are shown in Figure 8, Figure 9 and Figure 10 respectively. The plots define a linear correlation with regression line of

Akatsi: $\delta^2H = 7.177\ \delta^{18}O + 6.94$ (n=23; R^2=0.864) (15)

Amedzofe: $\delta^2H = 7.212\ \delta^{18}O + 7.07$ (n=51; $R^2=0.921$) (16)

Kpando: $\delta^2H = 7.187\ \delta^{18}O + 8.96$ (n=35; $R^2=0.965$) (17)

The physical basis for this correlation lies in the fractionation of isotopes during evaporation-condensation processes (Gourcey et al., 2005).

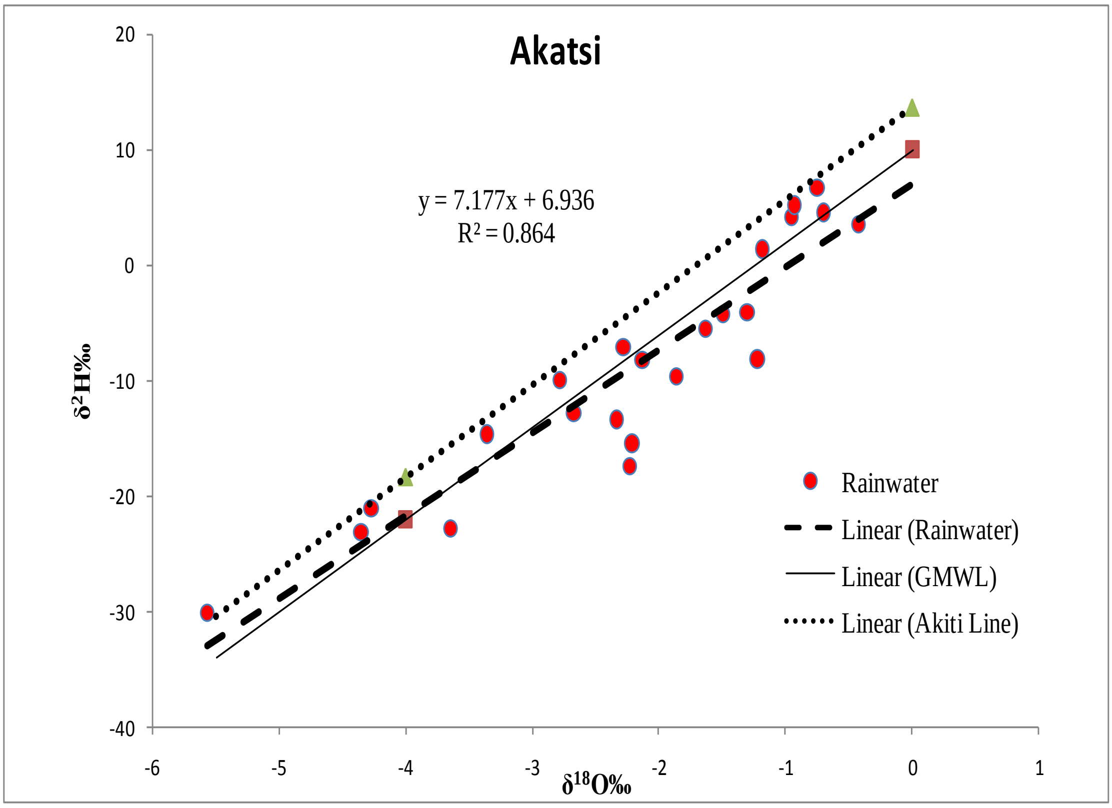

Fig 8: The relationship between δ^2H and $\delta^{18}O$ in rainfall at Akatsi

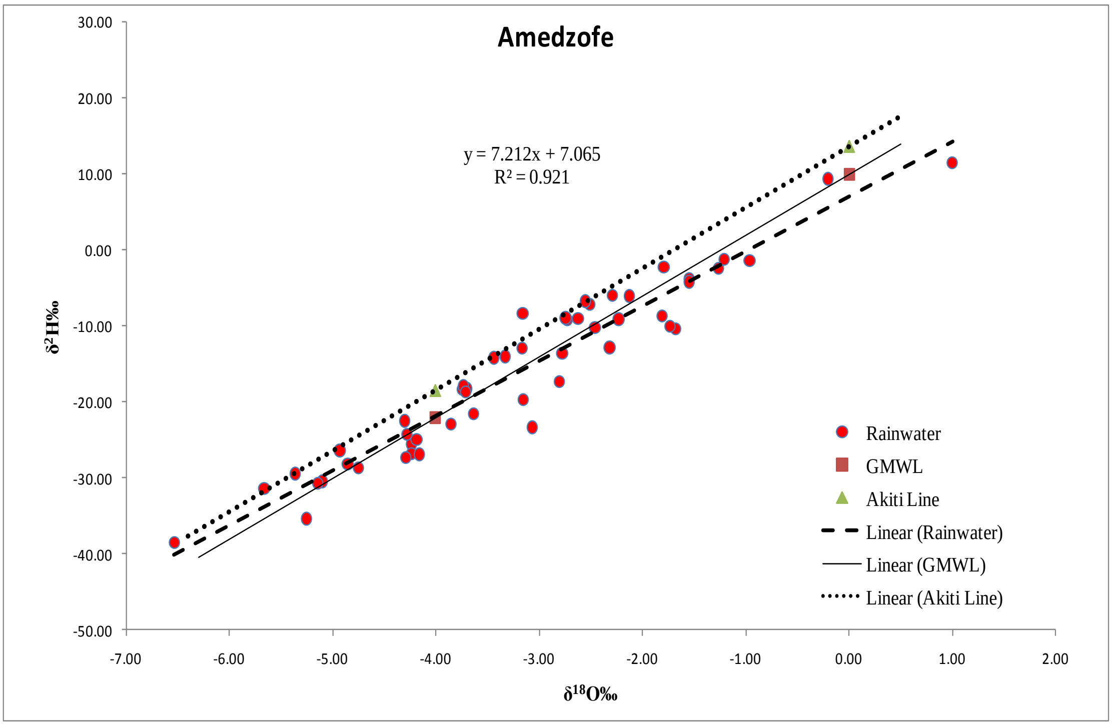

Fig 9: The relationship between δ^2H and δ^{18}O in rainfall at Amedzofe

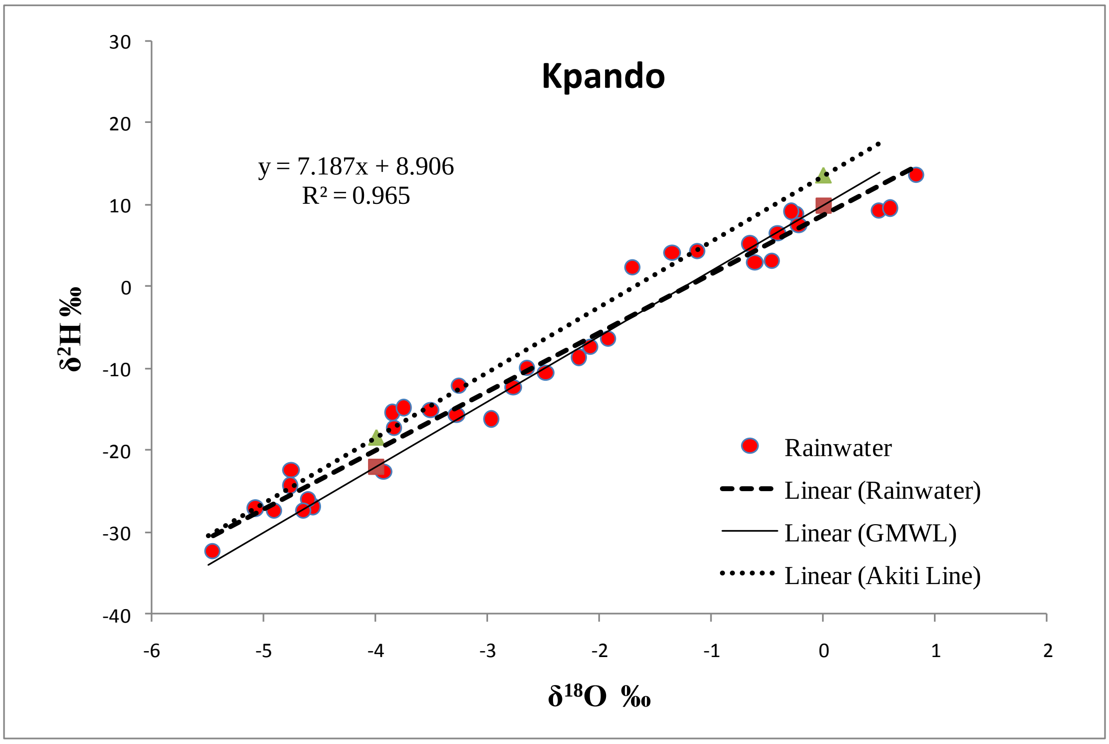

Fig 10: The relationship between δ^2H and δ^{18}O in rainfall at Kpando

Comparing the LMWL developed by Akiti (1980) with the Akatsi, Amedzofe and Kpando, the slope of the three stations are slightly lower. The stable isotopes of a given area is controlled by local climatic factors, and may differ from the GMWL, $\delta D = 8\ \delta^{18}O+10$, developed by Craig (1961) and LMWL $\delta D = 7.86\ \delta^{18}O+13.62$ developed by Akiti (1980). The GMWL and LMWL is actually an average of many LMWLs controlled by local climatic parameters, including the origin of the vapour mass, re-evaporation during rainfall and the seasonality of precipitation (Clark and Fritz, 1997). The three sampling points are located in the coastal, mountainous and forest environments and are characterized by intense rainfall and evaporation, therefore secondary evaporation during rainfall is expected. When it is raining through a dry air column, some will evaporate leading to the shift of the stable isotopes away from the GMWL (Friedman et al (1962). This phenomenon has been observed in several areas especially in arid regions (Clark, 1987; Dansgaard, 1964).

Compared with the LMWL, the slope of the Akatsi, Amedzofe and Kpando, are lower, which indicates the occurrence of secondary evaporation during rainfall. This effect is greatest for light rains. Once the air column is water-saturated, such secondary evaporation is diminished. Therefore, the slope of the meteoric water lines for heavy rainfall will be close to that of the LMWL. Thus, meteoric water lines were developed for heavy rainfall events greater than 10 mm.

Akatsi: $\delta^2H = 6.783\ \delta^{18}O + 6.208$ ($n=17$; $R^2=0.953$), Rain>10mm (18)

Amedzofe: $\delta^2H = 7.944\ \delta^{18}O + 9.856$ ($n=36$; $R^2=0.906$). Rain>10mm (19)

Kpando: $\delta^2H = 7.538\ \delta^{18}O + 10.45$ ($n=21$; $R^2=0.943$), Rain>10mm (20)

The results show that the slope of the meteoric water line for Akatsi, Amedzofe and Kpando are 6.78, 7.94 and 7.54 respectively for rainfall greater than 10 mm. Additionally, with the exception of Akatsi, the slope of Kpando and Amedzofe are closer to the slope of 7.86 obtained by Akiti (1980) and 8 obtained by Craig (1960) with the increase of the intensity of rainfall. A further consideration of rainfall greater than 20mm yields the following equations

Akatsi: $\delta^2H = 6.715\,\delta^{18}O + 5.730$ ($n=11$; $R^2=0.933$), Rain>20mm (21)

Amedzofe: $\delta^2H = 8.213\,\delta^{18}O + 11.26$ ($n=24$; $R^2=0.924$). Rain>20mm (22)

Kpando: $\delta^2H = 8.09\,\delta^{18}O + 13.28$ ($n=8$; $R^2=0.7$). Rain>20mm (23)

The Amedzofe and Kpando yield slopes of 8.21 and 8.09 respectively. These slopes are approximately equal to slope of 8 (Craig, 1960).

The plot of $\delta^{18}O$ and δ^2H for all the rainfall events at Akatsi, Amedzofe and Kpando are shown in Figure 11. The plots define a linear correlation with regression line of,

$\delta^2H = 7.258\,\delta^{18}O + 7.79$ ($n=109$; $R^2=0.932$) (24)

This equation (24) represents the Lower Volta Meteoric Water Line (LVMWL). Meteoric water lines were developed for heavy rainfall events greater than 10 mm and greater than 20 mm.

$\delta^2H = 7.395\,\delta^{18}O + 8.34$ ($n=77$; $R^2=0.920$). Rain > 10mm (25)

$\delta^2H = 7.453\,\delta^{18}O + 8.621$ ($n=45$; $R^2=0.907$). Rain > 20mm (26)

As observed earlier, elimination of rainfall amount less 10 mm and 20 mm yields slope closer to 8. Mook (2006) stated that the threshold of precipitation for the secondary evaporation to have an effect is 20 mm/month. Similarly, Clark (1987) found that, excluding rainfall events less than 20 mm yields the slope of the LMWL around 7.8, similar to the equilibrium value of 8. This study indicates that the threshold of 20 mm is a good estimate and applicable in the study area, hence, in the lower Volta, data for rainfall events greater than 20 mm orients the slope closer to 8.

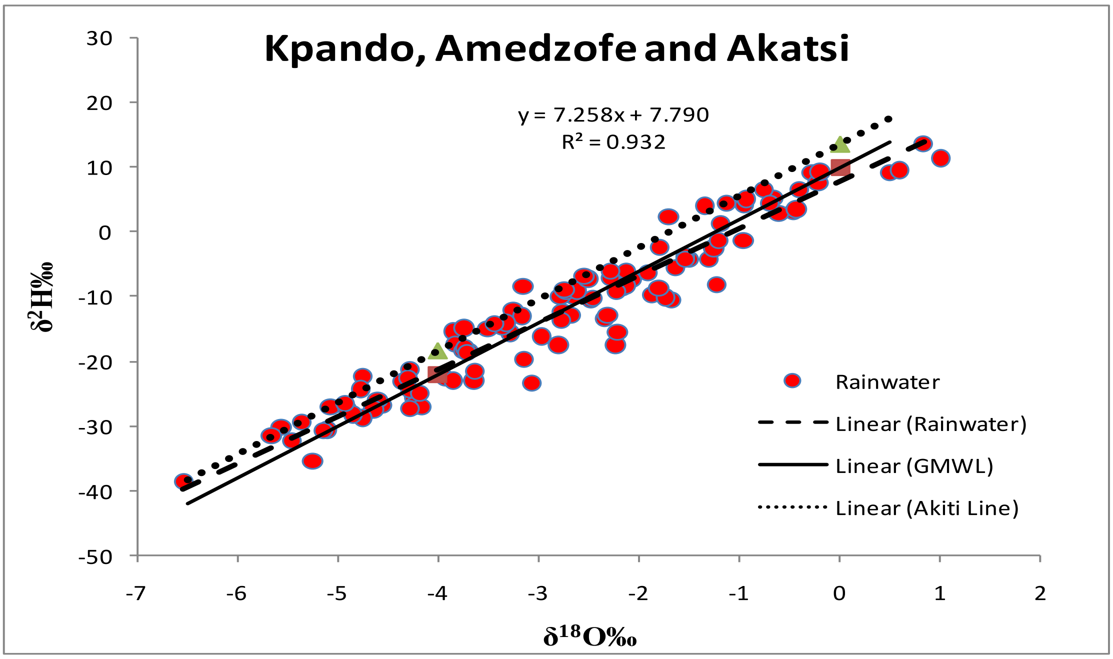

Figure 11: The relationship between δ^2H and δ^{18}O in rainfall at Kpando, Amedzofe and Akatsi.

4.4.1 ALTITUDE EFFECT ON THE STABLE ISOTOPES

The altitude effect, as likelihood for a systematic decrease of stable isotope composition (with increasing altitude), is theoretically associated with the concept that it is a function of the cooling of air masses as they rise to higher elevation. This effect has been largely used by several authors around the world as a tool to determine groundwater-recharge zones (Payne and Yurtsever, 1974; Fontes and Olivry, 1976; Gonfiantini et al., 1976, 2001; Yurtsever and Gat, 1981; Gasparini et al., 1990; Kattan, 1997b). Based on the correlations between the weighted means of both $\delta^{18}O$ and $\delta^{2}H$ and the corresponding altitude for all the meteoric stations, the least-squares regression lines were calculated for Akatsi - Amedzofe and Amedzofe - Kpando.

The calculated altitude effect shows a gradual lapse rate of $\delta^{18}O$ and $\delta\ ^{2}H$ of about -0.2‰/100 m and -1.5 ‰/100 m for Akatsi and Amezofe respectively. Amedzofe and Kpando showed an altitude effect of -0.15‰ /100 m. and -2 ‰/100 m for $\delta\ ^{18}O$ and $\delta\ ^{2}H$ respectively, (Figures 12, 13, 14 and 15). This effect varies slightly with the value of -0.13‰ obtained by Akiti (1980) from rainfall in Accra (35m) and Aburi (427m) above mean sea level. Studies by Fonte and Olivry, 1977 on the Cameroon mountains yielded an altitude effect of -0.16‰ per 100m for $\delta^{18}O$. Other studies around the globe by Yurtsever and Gat (1981) gave a $\delta^{18}O$ laps rate of between -0.15 and -0.5 ‰ per 100 m and $\delta^{2}H$ lapse rate of between -1.5 and -4‰ per 100 m. Kattan (1997) studied stable isotopes in precipitation over Syria and estimated an altitude effect of about -0.23 and -1.6‰ per 100 m, for $\delta\ ^{18}O$ and the $\delta\ ^{2}H$, respectively. Prizgonov et al. (1988) also provides an estimate of $\delta\ ^{18}O$ gradient of -0.19‰ per 100 m.

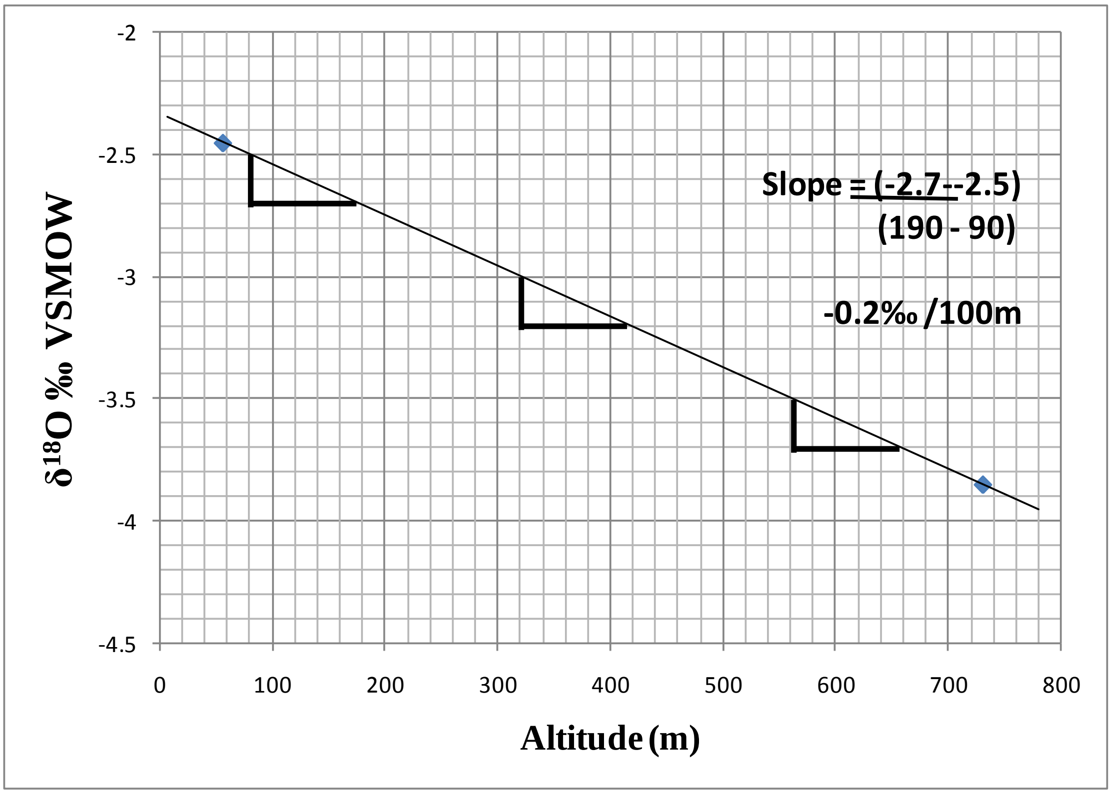

Figure 12: The relationship between altitude (m) and $\delta^{18}O$‰ VSMOW in Akatsi - Amedzofe

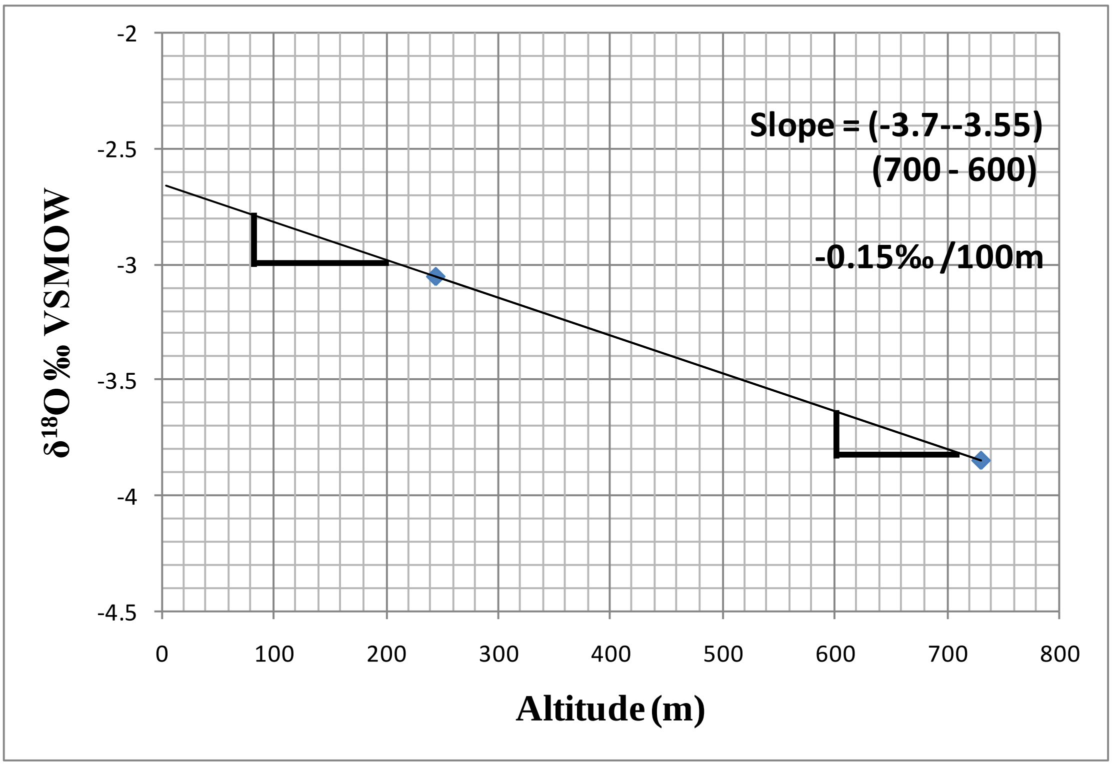

Figure 13: The relationship between altitude (m) and $\delta^{18}O$‰ VSMOW in Amedzofe – Kpando

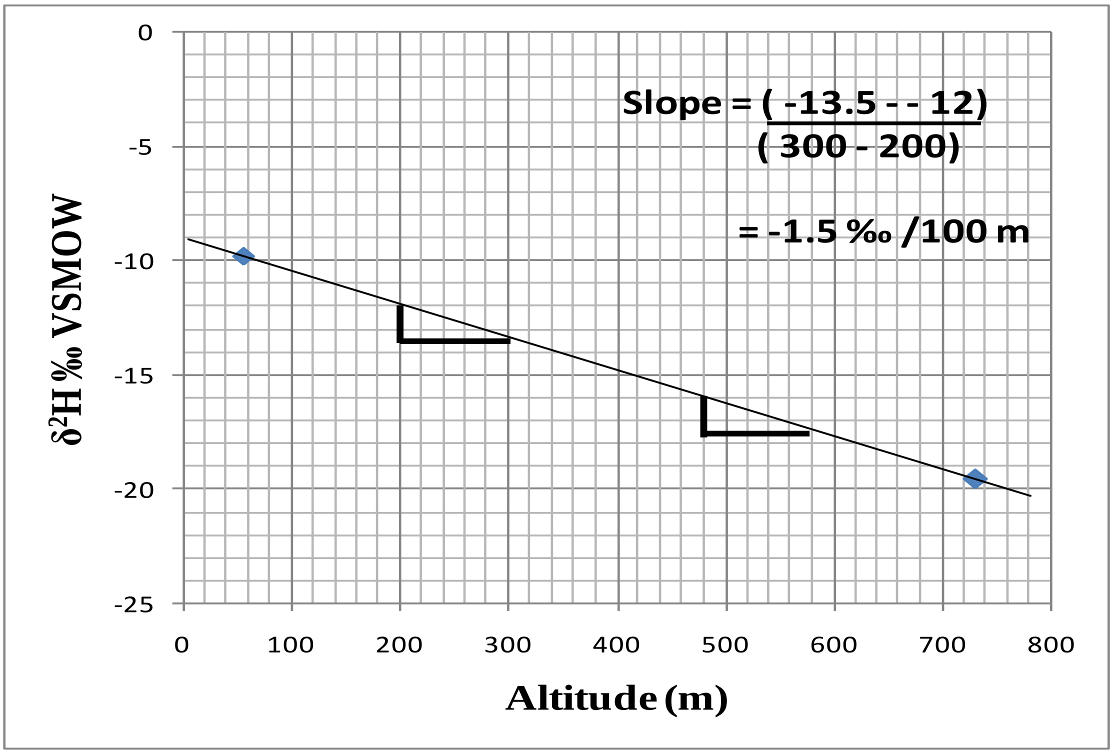

Figure 14: The relationship between altitude (m) and δ^2H‰ VSMOW in Akatsi - Amedzofe.

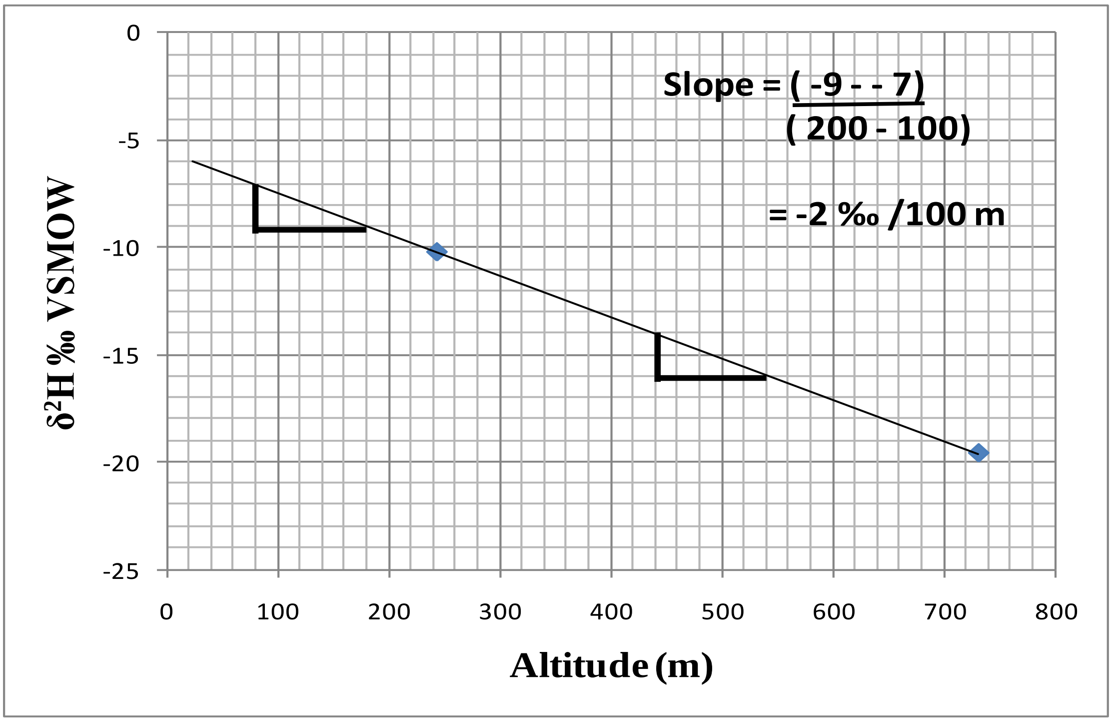

Figure 15: The relationship between altitude (m) and δ^2H‰ VSMOW in Amedzofe – Kpando.

Despite the high agreement of the results obtained with these studies, there is a slight variation with the values obtained by Akiti (1980) in Ghana especially with Akatsi - Amedzofe. The possible explanation to this anomaly is that, Akiti's (1980) estimate was based on a narrow range of altitude of about 394 m amsl (Accra coastal area with altitude of 35m and Aburi a mountainous area with altitude of 427m) while Akatsi (a coastal area with altitude of 56 m amsl and Amedzofe a mountainous area of 731 m amsl has a range of 675 m amsl . However, Amedzofe and Kpando with an altitude difference of 487 m amsl has an altitude effect of -0.15 ‰/100m close to the value of -0.13 ‰/100m obtained by Akiti (1980).

4.4.2 TEMPERATURE AND AMOUNT EFFECT ON THE STABLE ISOTOPES OF RAINFALL

Temperature is inversely related to the isotopic fractionation that occurs during condensation and evaporation (Mazor, 2004; Mook, 2006). As a result, precipitation normally has high isotopic values during warmer summers and low during cooler winters. The monthly weighted average of δ^{18}O, rainfall and mean temperature from the Akatsi, Amedzofe and Kpando are shown in Figure 16, Figure 17 and Figure 18. The three stations exhibit these typical seasonal variations in isotopic composition.

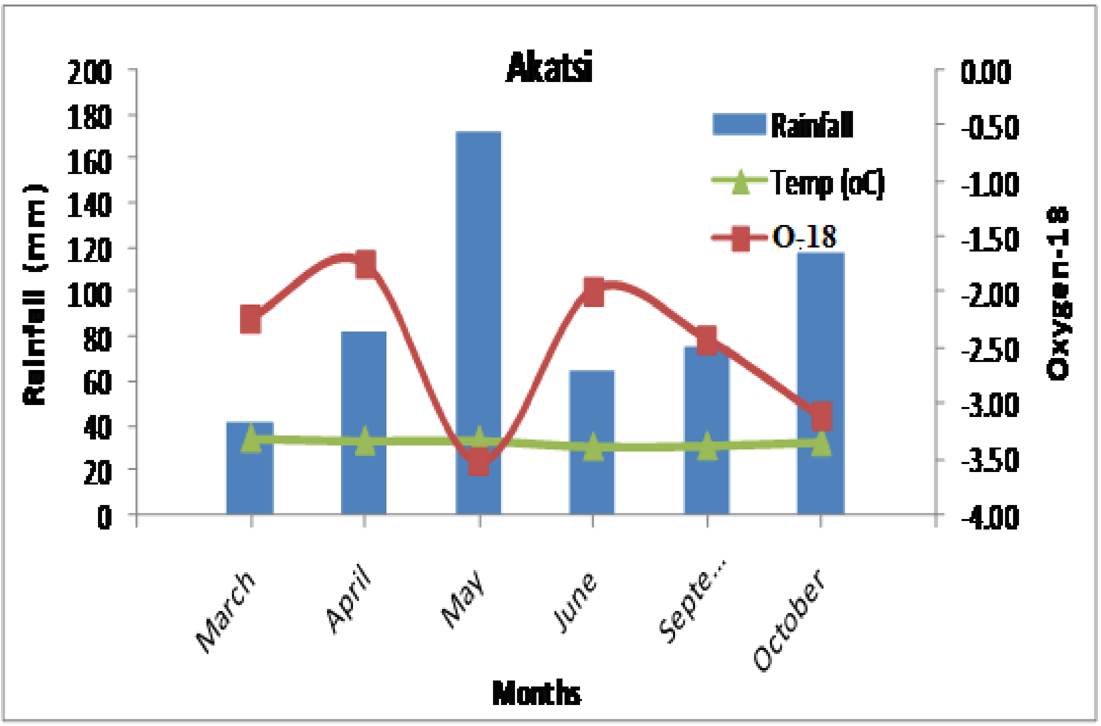

Figure 16: Temperature and amount effects on δ^{18}O of precipitation in the Akatsi.

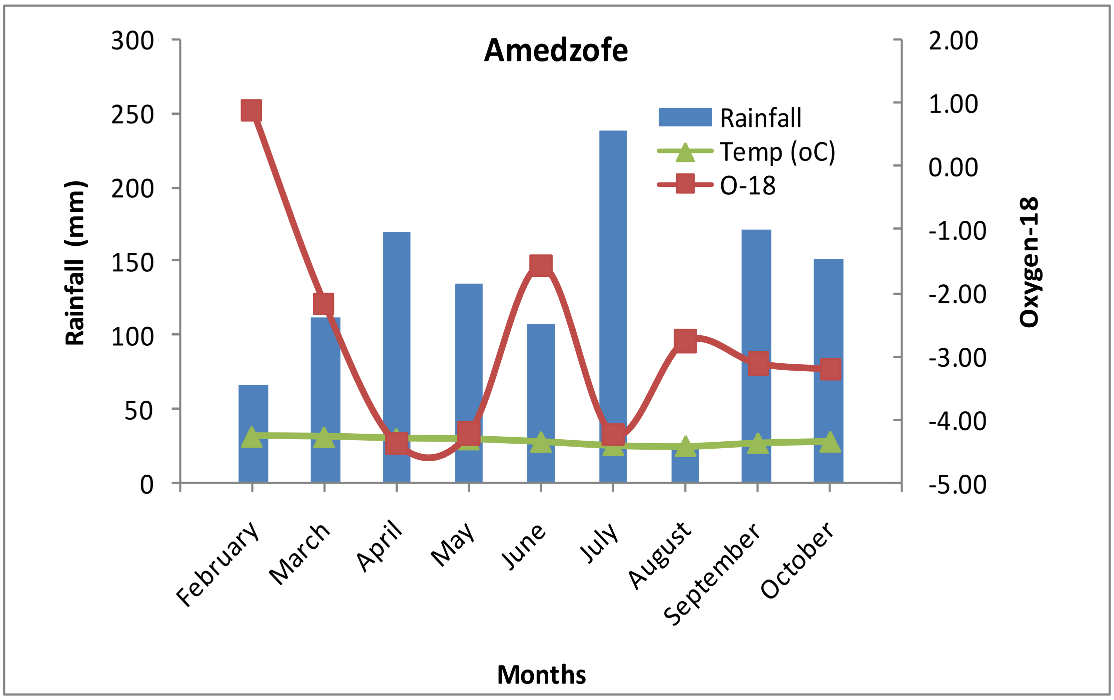

Figure 17: Temperature and amount effects on δ^{18}O of precipitation in the Amedzofe

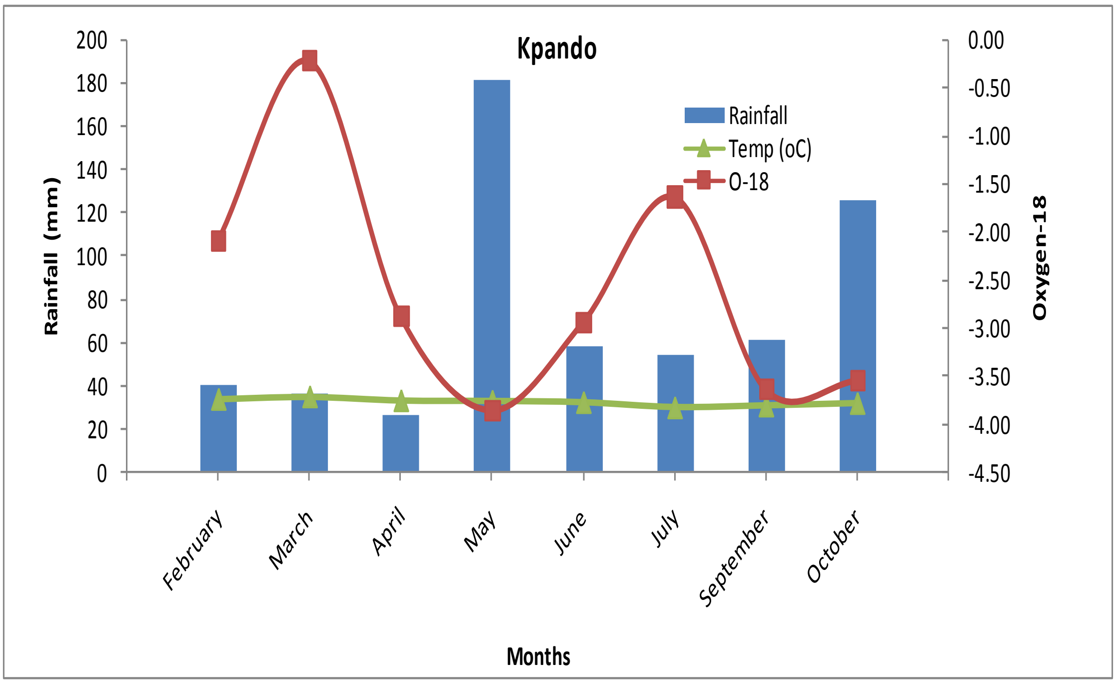

Figure 18: Temperature and amount effects on $\delta^{18}O$ of precipitation in the Kpando

It is interesting to note that, the most enriched and depleted samples are not associated with highest and lowest temperature in all the stations. There is a linear relationship between mean monthly surface temperatures (T) and $\delta^{18}O$ at each of the stations. A relationship can be described by the following least-squares-fit linear regression.

$\delta^{18}O = -0.052T_{montly}-0.976‰$ $(R^2=0.006)$ Akatsi (27)

$\delta^{18}O = -0.058T_{montly}-2.361‰$ $(R^2=0.009)$ Amedzofe (28)

$\delta^{18}O = 0.304T_{montly}-11.45‰$ $(R^2=0.073)$ Kpando (29)

The variation pattern of isotope composition is inconsistent with the temperature. This could be due to narrow range in temperature (about ~4^{o}C) in all the stations. The weak correlation of $\delta^{18}O$ and temperature suggest that, temperature may not be the only factor controlling the isotope fractionation.

For this reason, the relation between $\delta^{18}O$ and rainfall amount for the three stations was also examined and shown in Figures 19, 20 and 21.

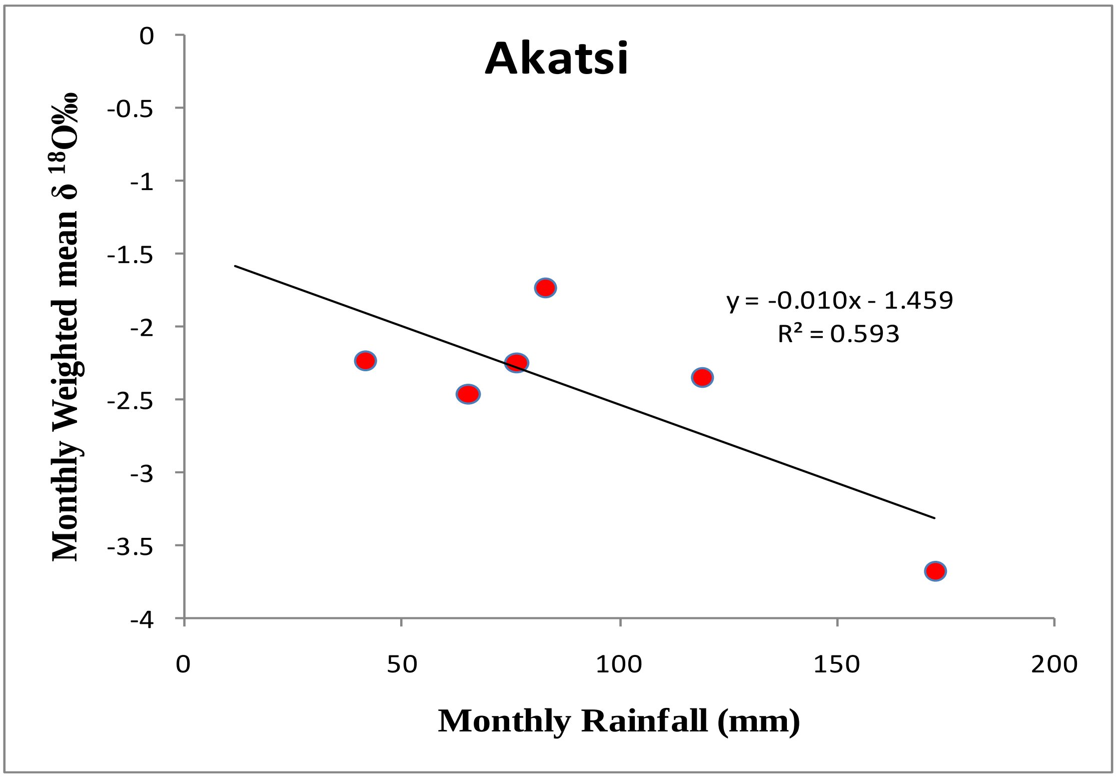

Figure 19: The relationship between monthly rainfall and monthly weighted mean $\delta\ ^{18}O$ ‰ VSMOW in Akatsi

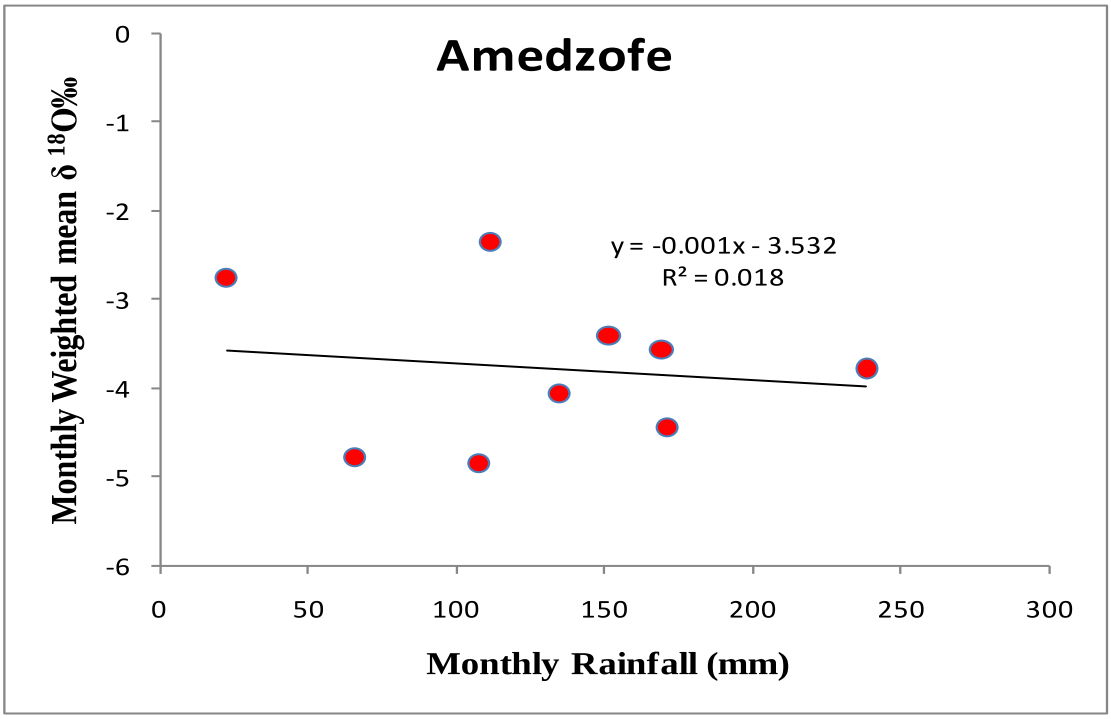

Figure 20: **The relationship between monthly rainfall and monthly weighted mean δ ^{18}O ‰ VSMOW in Amedzofe**

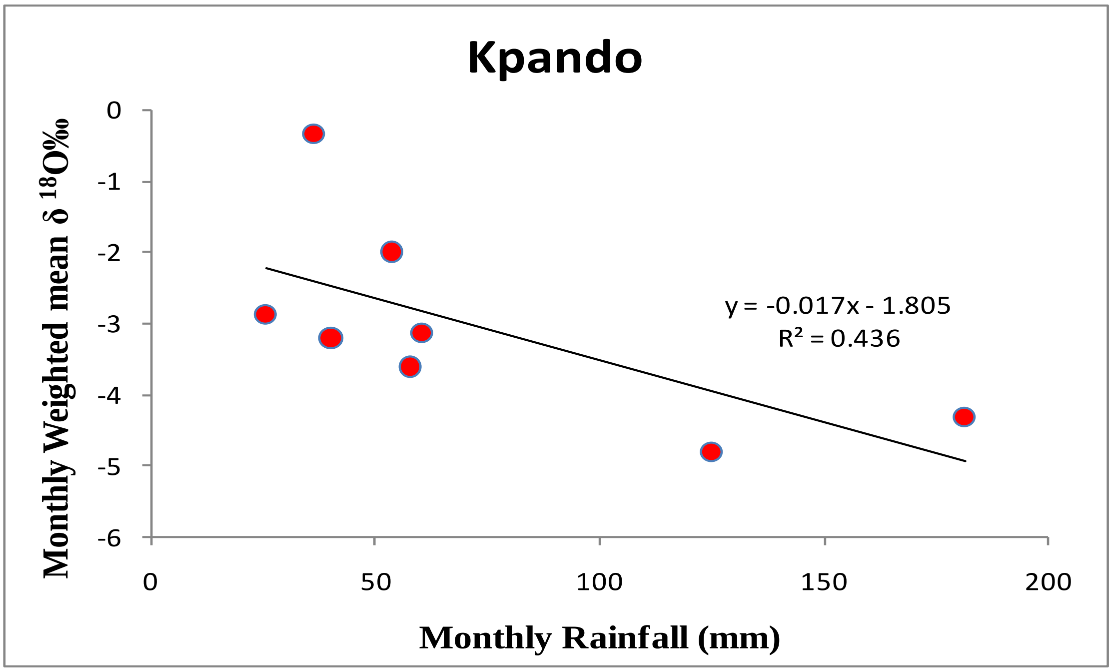

Figure 21: **The relationship between monthly rainfall and monthly weighted mean δ ^{18}O ‰ VSMOW in Kpando**

There is a very good correlation between the average monthly precipitation (P) and $\delta^{18}O$ at Kpando and Akatsi, while Amedzofe showed a weak correlation. The three stations define the best fit equations as:

$\delta^{18}O = -0.017P_{montly}-1.804‰$ ($R^2=0.436$) Kpando (30)

$\delta^{18}O = -0.010P_{montly}-1.459‰$ ($R^2=0.593$) Akatsi (31)

$\delta^{18}O = -0.001P_{montly}-3.532‰$ ($R^2=0.018$) Amedzofe (32)

This indicates that the amount effect is the dominant process controlling the rain stable isotopes in Akatsi and Kpando while Amedzofe is primarily controlled by the altitude effect.

4.5 GROUNDWATER CHEMISTRY

4.5.1 PHYSICAL PARAMETERS IN GROUNDWATER

The pH of the groundwater at Akatsi ranged from 5.13 to 6.37 with a mean of 5.83. Amedzofe ranged from 5.07 to 96.94 with a mean of 6.07. Kpando ranged from 5.95 to 6.94 with a mean of 6.42. The conductivitiy and TDS recorded at Akatsi ranged from 103 to 726 µS/cm with a mean of 280.2 µS/cm and 55.5 to 363 mg/L with a mean of 224.9 mg/L. Amedzofe on the other hand had Conductivity and TDS ranging from 44.9 to 822 µS/cm with a mean of 280.2 µS/cm and 23 to 408 mg/L with a mean of 140 mg/L. Kpando had both the conductivity and TDS ranging from 318 to 1163 µS/cm with a mean of 683.5 µS/cm and 159 to 581 mg/L with a mean of 341 mg/L.

4.5.2 CHEMICAL PARAMETERS IN GROUNDWATER

Na^+ and K^+ concentrations in Akatsi varied between 100.8 to 292.0mg/L with a mean of 187.3mg/L and 2.0 to 50 mg/L with a mean of 11.8mg/L respectively. Amedzofe had Na^+ and K^+ concentrations ranging from 12.7 to110.7mg/L with a mean of 45.0mg/L and 0.1 to 60.2mg/L with a mean of 21.6mg/L respectively. Kpando also had respective Na^+ and K^+ concentrations ranging from 94.2 to 360.7mg/L with a mean of 162.7mg/L and 3.0 to 36.4 mg/L with a mean of 11.2mg/L.

Ca^{2+} and Mg^{2+} concentrations recorded at Akatsi ranged from 12 to 4081mg/L with a mean of 692.9mg/L and 0.51 to 1.21mg/L with a mean of 0.87mg/L respectively. In Amedzofe they ranged from 2.4 to 15.2mg/L with a mean of 5.2mg/L and 0.07 to 1.3mg/L with a mean of 0.51mg/L respectively. Kpando had concentrations ranging from 4.81 to 24.05mg/L with a mean of 10.82mg/L and 0.37 to 1.2mg/L with a mean of 0.88mg/L respectively.

Chloride (Cl^-) in groundwater mostly originates from ancient seawater entrapped in sediments, halite dissolution and related minerals in evaporite deposits. Chlorides in groundwater can also be as a result of concentration by evaporation of chloride contributed by precipitation and fallout from the atmosphere as aerosol sprays (Davies and Dewiest, 1996). Very high chloride content may impart saline taste to groundwater, which may affect its suitability for drinking purposes. High chloride values in surface water can be attributed to the presence of faecal matter.

Another important source of chloride may be from volcanic waters in hot springs system. Mazor (1997) suggested that seawater intrusion a few meters from the coast is a possible source of chloride in groundwater. White (1974) outlined that Cl^- in groundwater can be used as good tracer to follow processes of groundwater contamination/salinisation, especially during initial stage to monitor seawater/freshwater interface movements. The maximum permissible level of chloride in drinking water is 250mg/L (WHO, 1984).

In Akatsi the Cl^- concentration ranged from 81.97 to 173.95mg/L with a mean of 145.07mg/L. Amedzofe ranged from 13.99 to 117.96mg/L with a mean of 38.94mg/L. Kpando ranged from 25.99 to 73.98mg/L with a mean of 56.02mg/L.

Nitrate (NO_3^-) is a widespread contaminant in ground and surface waters. High concentrations in groundwater are of major concern in many parts of the world.

In Ghana, nitrate concentrations have been rising in many locations over recent decades, but the current rising trends have been attributed primarily to diffuse pollution from intensive farming by application of nitrate fertilizers. Mallari, (1959) did a pioneering work in the Upper East Region and compiled a list of nitrate levels in the region prior to 1959 and found that only one well in his selected samples had nitrate concentration above 9mg/L, this he attribute to local pollution.

Akiti (1982) later investigated the level of nitrates in the Upper West Region of Ghana and concluded that the high concentrations were due to the following factors,

- Animal excrement resulting from cattle rearing.
- Fixation of nitrogen by certain plants.
- Agricultural fertilizer application.

Ganyaglo (2006) observed that high nitrate concentrations in some ground waters in parts of Eastern region of Ghana may be due to well-head pollution as a result of poor sanitations around the wells.

Direct application of nitrate to land as an agricultural fertilizer is not the only source. Atmospheric deposition, discharge from septic tanks and leaking sewers, the spreading of sewage sludge to land and seepage from landfills can all contribute to the pollutant load (Wakida and Lerner, 2005). Upper limit of nitrate in drinking water in the USA, Canada and Australia is 10 mg/L. Excess nitrate concentrations can also cause eutrophication, which enriches water body by increasing levels of nutrients such as nitrogen and phosphorus (Mason, 2002). High nutrient levels in water affect biodiversity by favouring plants which need or can survive in nutrient-rich environments, and can lead to excessive plant growth (WHO, 1999), typical example is the algae.

The NO_3^- concentration recorded in Akatsi groundwater ranged from 0.17 to 1.05mg/L with a mean value of 0.54mg/L. Amedzofe ranged from 0.03 to 0.96mg/L with a mean of 0.35mg/L and Kpando ranged from 0.11 to 1.05mg/L with a mean of 0.43mg/L.

Sulphur is an essential nutrient for vegetation. It is also an essential element for seawater and marine sediments. Its four main oxidation states raging from +IV to –II making it both electron acceptor and donor in redox reaction. The major forms of sulphur in subsurface water include sulphate and sulphide minerals, dissolved sulphate (SO_4^{2-}) dissolved sulphide (HS^-) and hydrogen sulphide gas (H_2S). Organic sulphur is a component of organic compounds such as humic substances, kerogen and hydrocarbons. Its oxidation and recycling in soil produces ‘’terrestrial’’ sulphate found in semi-arid regions. Atmospheric sulphur sources include natural and ‘’technogenic’’ or industrial SO_2, particulate sulphur and aerosol (Chapman, 1992) Sulphur compounds from these various sources contribute in the geochemical evolution of groundwater. They also add to groundwater salinisation. The maximum permissible limit of sulphate in drinking water is 400mg/L (WHO, 1984).

SO_4^{2-} concentration recorded at Akatsi varied between 7.28 and 50.68mg/L with a mean of 31.77mg/L. Amedzofe ranged from 9.81 to 55.34mg/L with a mean of 18.85mg/L whilst Kpando ranged from 1.55 to 49.71mg/L with a mean of 20.69mg/L.

Decay of organic matter in the root zone produce CO_2 which when reacted with water can produce carbonic acid. Furthermore, atmospheric CO_2 can react with water in the atmosphere to produce carbonic acid. In natural conditions, carbonic acid (H_2CO_3) formed from interaction of atmospheric CO_2 with water (H_2O) reacts with $CaCO_3$ present in soil to form Ca^{2+} and HCO_3^- ions, as shown in the equation 33 and 34 below

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (33)$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^- \qquad (34)$$

The H_2CO_3 can also dissolve the minerals present in the flow path of groundwater. The solution products of silicate weathering are more difficult to quantify, because the degradation of silicates is dissimilar, generating a variety of solid products, such as clays (Davies and Dewiest, 1966). A general reaction for weathering of silicate rocks with H_2CO_3 can be written as:

$$(Na^+ ; Mg^{2+} ; Ca^{2+} ;K^+) \text{ silicates} + H_2CO_3 \rightarrow H_4SiO_4 + HCO_3 + Na^+ + Mg^{2+} + Ca^{2+} + K^+ + \text{Clays} \qquad (35)$$

Bicarbonate in groundwater can also be obtained from dissociation of sodium bicarbonate ($NaHCO_3$) and calcium bicarbonate ($CaHCO_3$) formed from weathering of plagioclase feldspars. This dissociation normally occurs in the presence of weak carbonic acid from rain as shown in equation 36

$$NaHCO_3 + H_2CO_3 \rightarrow Na^+ + HCO_3^- \qquad (36)$$

HCO_3^- concentration recorded at Akatsi ranged from 58.52 to 204.82mg/L with a mean of 126.79mg/L. Amedzofe ranged from 29.26 to 360.88mg/L with a mean of 136.55mg/L and Kpando ranged from126.79 to 604.71mg/L with a mean of 344.62mg/L.

4.6 STABLE ISOTOPES COMPOSITION OF GROUNDWATER

Taking into account all data, the statistical summary of the groundwater stable isotopes are presented in Table 7. The distribution of $\delta^{18}O$ ranges from -3.66 to -2.03‰, -3.59 to -3.45 and -3.14 to -2.07 while δ^2H ranges from -13.89 to -8.02‰, -16.47 to -15.20 and -6.53 to -8.24 for Amedzofe, Akatsi and Kpando respectively. The respective mean values of $\delta^{18}O$ are -3.02, -3.43 and -2.68 while δ^2H are -10.86, -16.07 and -8.24. The values of $\delta^{18}O$ and δ^2H in Akatsi are very narrow suggesting a homogeneous system while that of Kpando are isotopically enriched and have a broader distribution. The Amedzofe samples are generally depleted.

Table 7. Statistical summary of the groundwater $\delta^{18}O$ and δ^2H in Akatsi, Amedzofe and Kpando

	Amedzofe			Akatsi			Kpando		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
$\delta^{18}O$	-3.66	-2.03	-3.03	-3.59	-3.24	-3.43	-3.14	-2.07	-2.68
δ^2H	-13.89	-8.02	-10.86	-16.47	-15.20	-16.07	-10.25	-6.54	-8.24

Figures 22, 23 and 24 show the relation between $\delta^{18}O$ and δ^2H in the three stations. Included in the graph are the monthly weighted mean of $\delta^{18}O$ and δ^2H, Akiti line and LVMWL for all the stations. The δ^2H is linearly and positively correlated to the $\delta^{18}O$. The groundwater in the three sampling areas plotted on or between the LVMWL and

Akiti line. This suggests that the ground waters in the areas are of meteoric origin. The Amedzofe samples comprises of five spring waters and four ground waters. Three of the ground waters were samples at Matse-Dzokpe, Dzolo-Gbogame and Dzolokpuita, these communities show distinct stable isotopes from the spring water. However, the Avatime-Biakpa groundwater plot with the spring waters sampled at Avatime-Vane and Amedzofe. This observation indicates that, the groundwater in Avatime-Biakpa which is at the foot of the Amedzofe Mountain is receiving significant amount of recharge from the springs.

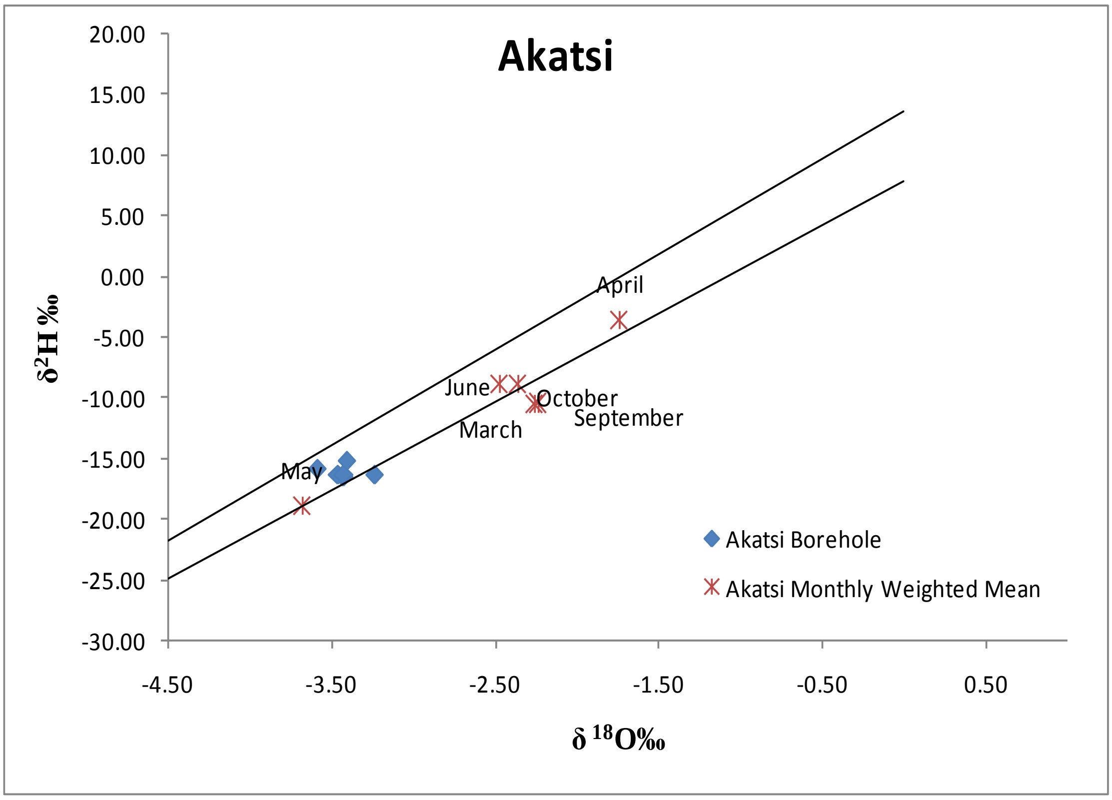

Figure 22: The relationship between δ^2H and δ ^{18}O in groundwater in Akatsi

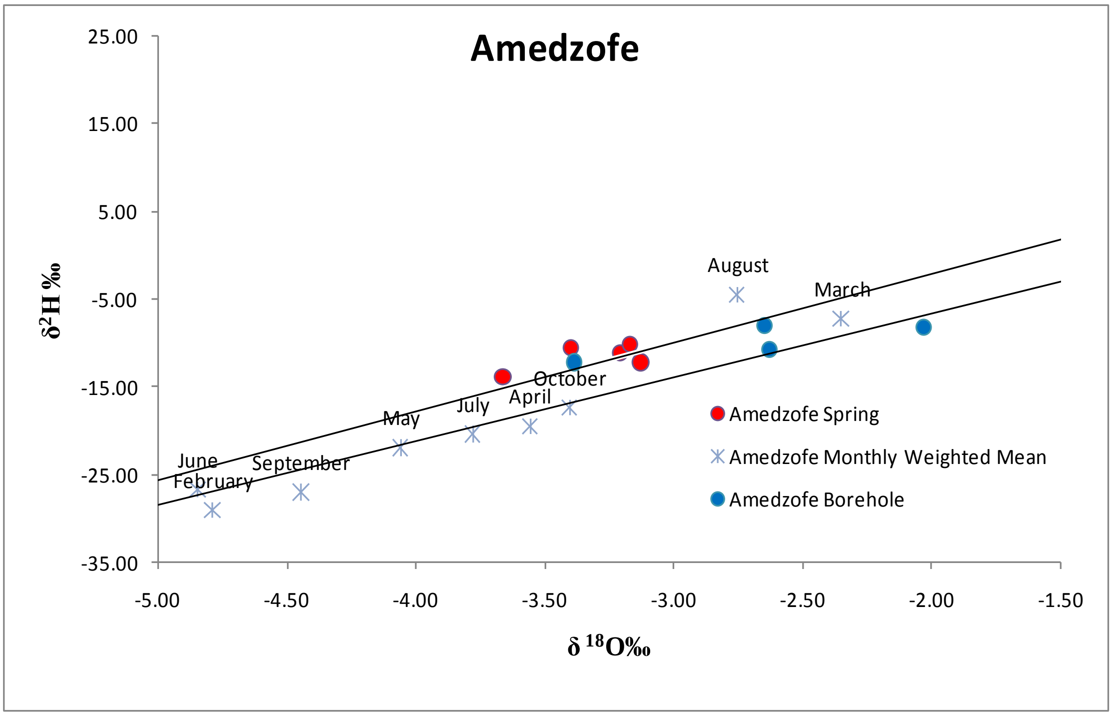

Figure 23: The relationship between δ ^{2}H and δ ^{18}O in groundwater in Amedzofe.

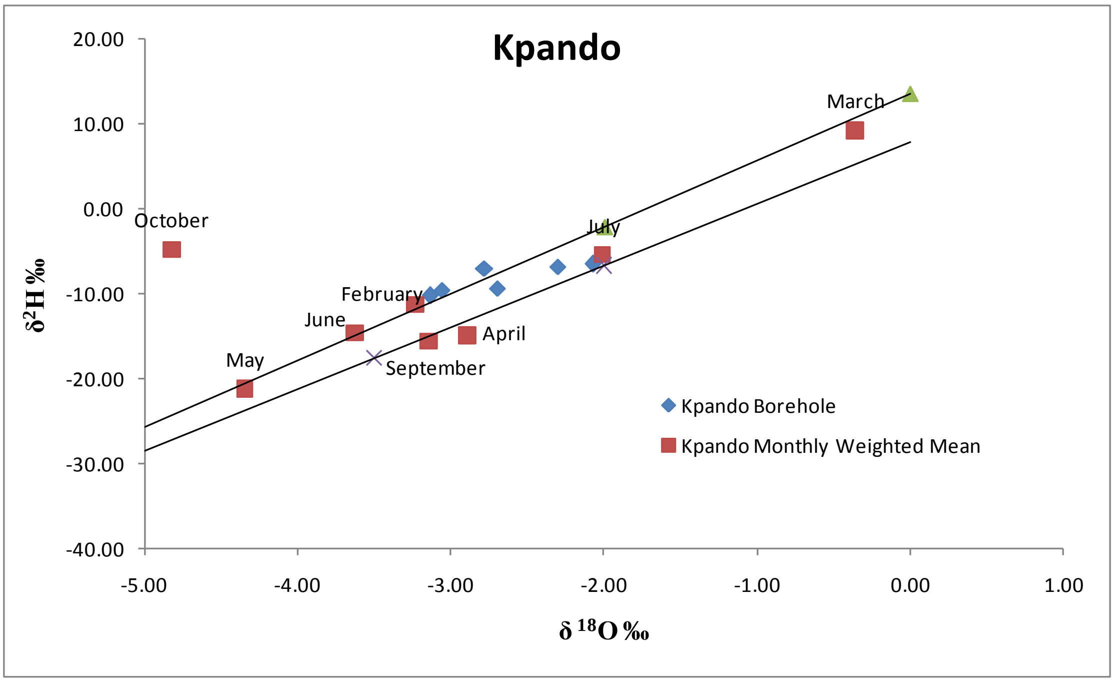

Figure 24: The relationship between δ^{2}H and δ ^{18}O in groundwater in Kpando

The weighted monthly mean of rainwater when plotted with groundwater stable isotopes can provide a fair estimate of monthly recharge to groundwater. On the basis of this assumption, Akatsi with a limited data of five months rainwater isotopes only May contributes to groundwater recharge. In Amedzofe however, the month of groundwater recharge are March, April, August and October. The groundwater in Kpando receive significant recharge in the month of February, April, May and September while March, May and October rains do not contribute to recharge

4.7 SOURCES OF IONS IN THE RAINWATER AND GROUNDWATER

Conventionally, the sources of dissolved ions in water bodies could be deduced from the variation of the characteristic solute-concentration ratios such as Na^+/Cl^-, Ca_2^+/Mg^{2+}, SO_4^{2-}/Cl^-, Br^-/Cl^- etc. However, in certain situations water chemistry may undergo secondary changes such as ion exchange, oxidation and reduction, precipitation, evaporation etc, which make it very difficult to use the ion-ratio approach to identify the sources of these ions.

Stable isotopes of water (^2H and ^{18}O) being relatively invariant over time, are therefore, well suited to study the complexities of groundwater hydrology in an area. Groundwater undergoing evaporation will have a positive correlation between $\delta^{18}O$ and conductivity while groundwater undergoing dissolution will have an increase in conductivity without a simultaneous increase or enrichment of $\delta^{18}O$.

Figure 25 shows the relationship between $\delta^{18}O$ and Conductivity in the Akatsi, Kpando and Amedzofe. The plot shows no correlation for the points suggesting evaporation is not the main source of ions in the rainwater. The Akatsi rainwater showed higher EC as compared to the rainwater in Kpando and Amedzofe. This EC in Akatsi rainwater could be due to;

(i) Akatsi is close to the sea, hence sea aerosols could be responsible for the high EC

(ii) Akatsi is sandwich between Tema and Lome. These are industrial towns in Ghana and Togo which release lots of pollutants in the atmosphere; hence the high EC could be due to the dissolution of these pollutants in the rain.

These effects however diminish as one moves away from the coast with Amedzofe showing little of this effect.

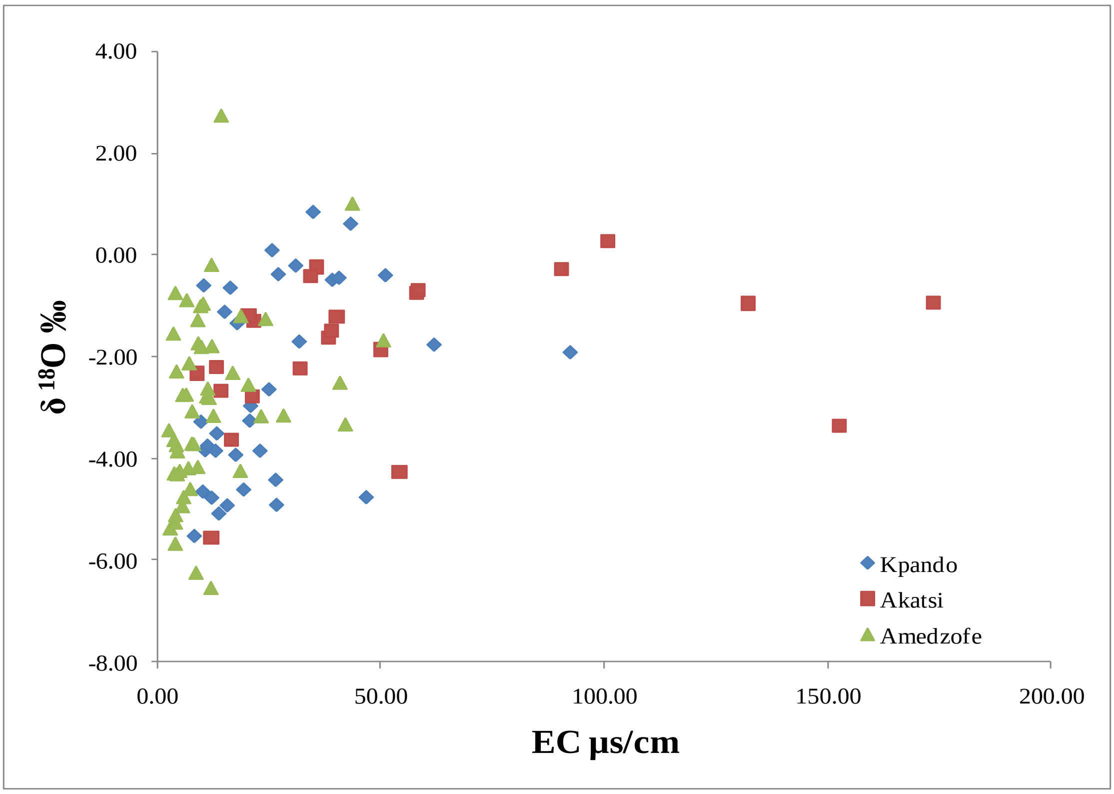

Figure 25: Relationship between rainwater δ^{18}O ‰ VSMOW and Conductivity in the three stations.

Similar plot of δ^{18}O ‰ VSMOW and Conductivity was made for the groundwater in the areas to determine their source of salinity. This is shown by Figure 26. The Kpando groundwater shows a weak correlation (R^2=0.02) suggesting evaporation is not the dominant factor controlling the groundwater in the area. Amedzofe on the other hand shows a positive strong correlation (R^2=0.86) between δ^{18}O ‰ VSMOW and Conductivity. This observation is due to the fact that, most samples from Amedzofe are spring waters, hence are exposed to the atmosphere thereby subject to evaporation. In the Akatsi, the groundwater shows an increase in conductivity without a simultaneous increase or enrichment of $\delta^{18}O$. It has already been established that, the Akatsi rainwater contains sea aerosols (NaCl), hence the soils in the area contains salts (NaCl). It follows from this thought that, the groundwater salinization is as a result of dissolution.

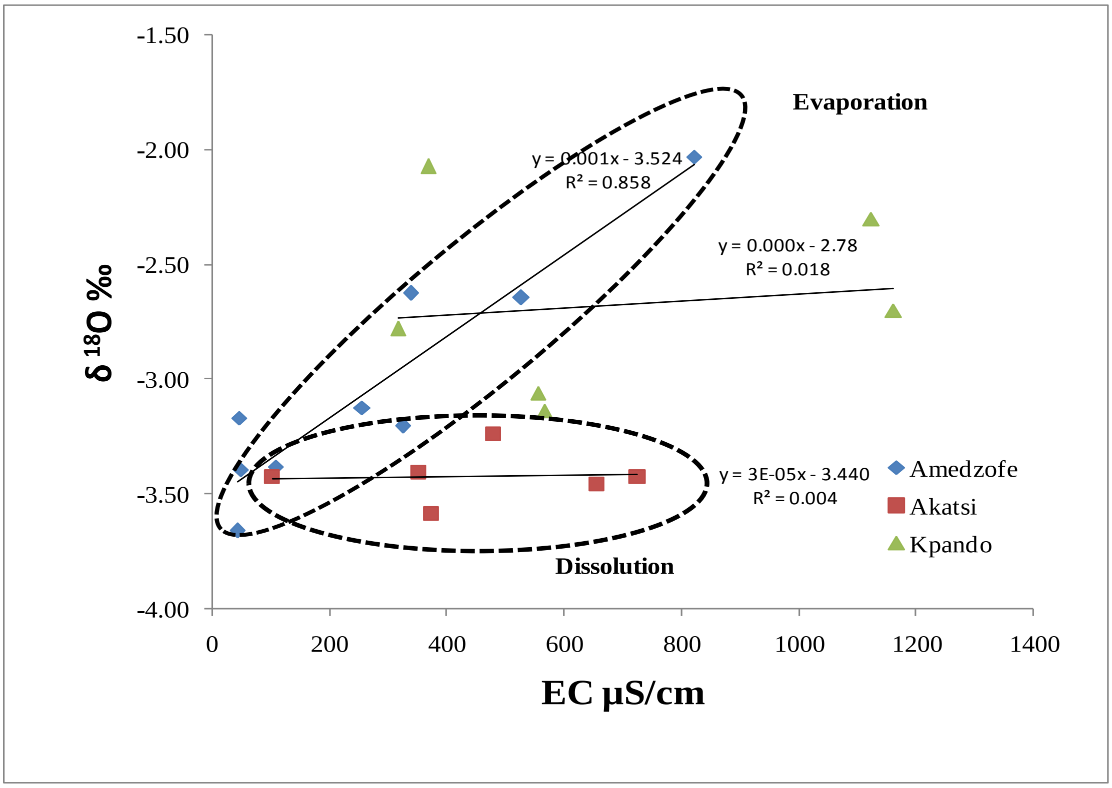

Figure 26: Relationship between groundwater $\delta^{18}O$ ‰ VSMOW and Conductivity in the three stations.

CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

This chapter draws from the analysis and discussions made in terms of the results in arriving at conclusions and recommendations for the study.

5.1 CONCLUSION

The chemical and isotopic composition of precipitation in Akatsi, Amedzofe and Kpando in the Volta region of Ghana has been investigated. The chemistry of the rainwater in the three stations shows some variations in both physical and chemical parameters. The observed pH values of rainwater at Amedzofe have an average value of 5.38 as compared to 6.19 and 5.6 for Akatsi and Kpando respectively. EC, TDS, turbidity and colour are generally low with higher values recorded at Akatsi while Amedzofe recorded the lowest values. Major ions concentrations and element-to-sodium ratios show clear variations with higher levels found in Akatsi (coastal zone) and lower levels found in Amedzofe. The chemical composition of rainfall in the coastal area (Akatsi) is influenced by ocean deposit from the Atlantic Ocean. Isotopic composition of rainwater in Akatsi (coastal area) presents high values of $\delta^{18}O$ and $\delta^{2}H$, whereas rainwater in the Amedzofe (mountainous area) was characterized by low values of $\delta^{18}O$ and $\delta^{2}H$. The Local Meteoric Water Line for the study area using rainfall greater than 20mm was defined as $\delta^{2}H = 7.453\ \delta^{18}O + 8.621$ (n=45; $R^2=0.907$, rain > 20mm). The stable isotopes of the three sampling points were found to be influenced by altitude and amount effect with temperature effect being insignificant. The calculated altitude effect shows a gradual lapse rate of $\delta^{18}O$ and $\delta^{2}H$ of about -0.2‰/100 m and -1.5 ‰/100 m for Akatsi and Amezofe respectively. Amedzofe and

Kpando showed an altitude effect of -0.15‰ /100 m. and -2 ‰/100 m for $\delta^{18}O$ and $\delta^{2}H$ respectively. The groundwater in the study area is mainly of meteoric origin with different months of recharge. The plot of $\delta^{18}O$ and EC shows that, mineral dissolution is the main factor controlling the groundwater salinization in Akatsi while Amedzofe and Kpando groundwater chemistry are mainly controlled by evaporation.

The trace elements found in the rainwater from the study area are generally low with the exception of Amedzofe rain which showed a high concentration of Cu.

5.2 RECOMMENDATION

Based on the study analysis carried out, the following recommendations are made

- The rainwater quality with respect to physico-chemical parameters is good, hence can be harvested and stored for domestic use.
- Rainwater stable isotopes monitoring in the area should be continued so as to obtain a larger data base for groundwater resources managements.
- Rainwater stable isotopes of other parts of Ghana should be carried out, preferably, Ghana should join the Global Network of Isotopes in Precipitation (GNIP).
- In the development of Local Meteoric water Line for Ghana, rainwater greater than 20 mm should be considered.

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APPENDICES

Apendix A: Physico-chemical paramerts of rainwater at Kpando

DATE	Rainfall Amount	pH	EC	TDS	SAL.	TSS	TEMP.	TURB.	COLOUR	Na^+	K^+	Ca^{2+}	Cl^-	OH^-	HCO_3	SO_4^{2-}	NO_3^-	Mg^{2+}
21/02/2013	7.20	5.75	50.80	25.60	0.00	4.00	24.10	5.00	16.00	11.30	1.50	2.24	15.49	40.00	48.76	17.09	0.29	0.67
25/02/2013	32.70	5.25	22.70	11.30	0.00	6.00	24.10	4.00	22.00	5.10	1.20	1.60	10.99	20.00	24.38	18.44	0.25	0.54
13/03/2013	4.70	4.79	25.40	12.70	0.00	8.00	24.10	3.00	24.00	4.30	1.50	2.88	20.49	10.00	12.19	17.67	0.28	0.76
15/03/2013	3.30	5.44	26.80	14.70	0.00	0.00	24.10	0.00	3.00	7.70	0.90	2.24	14.99	20.00	24.38	13.69	0.45	0.92
20/03/2013	6.20	5.99	30.70	15.80	0.00	8.00	24.10	3.00	21.00	3.40	1.10	2.24	7.99	30.00	36.58	32.43	0.45	0.83
21/03/2013	14.70	5.84	38.90	19.70	0.00	1.00	24.10	6.00	8.00	3.70	1.50	3.84	9.49	20.00	24.38	6.99	0.47	1.43
31/03/2013	7.20	5.81	40.40	20.30	0.00	3.00	24.10	2.00	5.00	5.90	3.90	3.52	13.99	20.00	24.38	17.96	0.32	1.54
09/04/2013	3.40	5.19	43.00	21.40	0.00	9.00	24.10	1.00	6.00	5.30	2.10	3.52	17.59	20.00	24.38	8.64	0.44	0.61
13/04/2013	2.30	5.83	34.60	20.20	0.00	5.00	24.00	2.00	11.00	4.80	1.60	4.16	19.49	20.00	24.38	12.43	0.25	1.07
25/04/2013	19.70	5.34	17.26	8.70	0.00	0.00	23.90	0.00	15.00	2.50	0.00	1.28	16.99	20.00	24.38	1.65	0.09	0.72
01/05/2013	6.40	5.84	11.11	6.20	0.00	2.00	23.90	0.00	0.00	2.00	2.50	1.60	16.39	10.00	12.19	9.71	0.18	0.87
03/05/2013	2.20	5.27	61.70	31.60	0.00	5.00	24.00	0.00	0.00	6.30	3.90	4.48	15.49	10.00	12.19	15.83	0.19	0.80
08/05/2013	12.70	5.40	13.01	6.60	0.00	0.00	24.00	0.00	0.00	2.60	2.10	2.24	11.99	20.00	24.38	5.44	0.61	0.72
10/05/2013	10.80	5.46	20.40	11.00	0.00	4.00	24.00	3.00	12.00	3.50	0.50	1.28	19.99	10.00	12.19	7.96	0.34	0.73
17/05/2013	9.40	5.14	26.40	13.30	0.00	7.00	23.90	4.00	15.00	5.60	1.60	2.24	12.49	20.00	24.38	4.56	0.36	0.73
18/05/2013	71.80	5.69	7.98	4.30	0.00	0.00	23.90	0.00	2.00	2.10	0.00	0.64	17.99	20.00	24.38	18.64	0.35	0.67
22/05/2013	40.90	6.00	10.41	5.80	0.00	0.00	24.00	5.00	12.00	1.40	0.00	1.28	12.79	20.00	24.38	9.71	0.34	0.82
28/05/2013	16.80	5.27	9.46	4.80	0.00	0.00	24.10	0.00	7.00	2.60	0.20	1.60	18.49	10.00	12.19	4.27	0.18	0.72
30/05/2013	10.40	5.61	46.50	23.90	0.00	6.00	24.00	5.00	10.00	4.90	1.60	5.12	17.59	20.00	24.38	11.55	0.37	0.47
01/06/2013	34.60	5.37	10.93	5.90	0.00	0.00	24.00	0.00	0.00	3.10	0.50	0.96	14.79	30.00	36.58	50.49	0.07	0.73
02/06/2013	4.90	5.76	92.20	46.80	0.00	2.00	23.90	6.00	24.00	24.50	5.30	4.48	12.49	40.00	48.76	73.20	0.46	0.64
08/06/2013	18.30	5.58	12.74	6.80	0.00	2.00	23.80	2.00	14.00	2.40	0.70	3.52	11.59	10.00	12.19	55.63	0.45	0.83
02/07/2013	15.30	5.60	20.60	10.30	0.00	1.00	24.00	9.00	24.00	5.90	2.10	2.40	13.10	16.00	19.51	12.72	0.25	0.52
04/07/2013	10.90	5.70	16.04	8.02	0.00	2.00	23.90	1.00	15.00	2.60	0.60	1.60	15.07	16.00	19.51	9.52	0.06	0.65
09/07/2013	11.40	5.70	14.77	7.39	0.00	2.00	24.10	2.00	8.00	2.60	0.50	1.60	14.19	16.00	19.51	3.10	0.07	0.45

14/07/2013	15.90	5.60	24.71	12.36	0.00	0.00	24.10	3.00	4.00	4.50	1.00	1.60	7.99	16.00	19.51	6.12	0.30	0.09
08/09/2013	24.20	5.60	9.89	4.93	0.00	0.00	23.80	4.00	6.00	2.30	0.70	2.40	11.39	16.00	19.51	19.42	0.14	0.78
09/09/2013	11.30	5.80	19.03	9.51	0.00	3.00	23.80	2.00	7.00	2.30	0.90	1.60	13.09	16.00	19.51	41.75	0.17	0.85
10/09/2013	3.30	5.70	31.49	15.75	0.10	7.00	23.70	0.00	0.00	6.30	1.50	1.60	16.49	16.00	19.51	18.86	0.36	0.79
21/09/2013	12.80	5.90	10.09	5.04	0.00	2.00	24.10	5.00	14.00	2.30	0.50	0.80	15.15	16.00	19.51	1.17	0.24	0.56
22/09/2013	8.80	5.80	17.58	8.79	0.00	5.00	24.00	3.00	5.00	1.60	0.00	2.40	17.09	8.00	9.75	27.18	0.14	0.72
03/10/2013	42.60	5.80	13.47	6.74	0.00	0.00	24.20	5.00	14.00	3.70	0.60	1.60	16.59	16.00	19.51	15.53	0.05	0.67
04/10/2013	24.40	5.70	11.87	5.94	0.00	0.00	24.10	0.00	5.00	2.20	0.30	1.60	11.99	32.00	39.01	4.85	0.44	0.89
06/10/2013	31.10	5.80	26.21	13.11	0.00	1.00	24.00	1.00	2.00	2.20	0.00	2.40	8.67	16.00	19.51	22.33	0.50	0.66
13/10/2013	26.80	5.70	15.35	7.68	0.00	0.00	24.10	2.00	7.00	2.50	0.40	2.40	10.59	16.00	19.51	13.98	0.16	0.71

Apendix B. Physico-chemical paramerts of rainwater at Akatsi

DATE	Rainfall Amount	pH	EC	TDS	SAL.	TSS	TEMP.	TURB.	Colour	Na$^+$	K$^+$	Ca^{2+}	Cl$^-$	OH$^-$	HCO$_3$	SO$_4^{2-}$	NO$_3^-$	Mg^{2+}
05/03/2013	41.5	5.98	31.7	16	0	12	23.9	6	30	6	2.4	2.88	16.99	10	12.19	73.1	0.894	0.79
26/04/2013	45.1	6.57	132.2	66.3	0.7	3	23.8	2	19	10.2	5.9	19.84	16.49	60	73.15	58.252	0.101	0.97
30/04/2013	37.7	5.74	13.99	7.7	0	0	23.9	5	8	4.1	1	0.64	17.49	20	24.28	49.709	0.537	1.07
11/05/2013	34.8	5.55	8.74	4.8	0	1	23.8	0	6	3.5	0.5	1.92	18.49	20	24.28	45.146	0.249	0.91
22/05/2013	22.1	5.62	12.93	6.8	0	3	23.9	2	11	3.6	0.3	1.92	19.49	20	24.28	55.631	0.76	0.78
26/05/2013	83	5.61	11.91	6.2	0	24	23.8	16	67	4.4	0.6	1.28	15.49	20	24.28	58.544	0.443	1.16
30/05/2013	32.6	6.05	21.3	11.7	0	10	23.9	6	28	5.8	2.5	2.24	20.49	20	24.28	52.039	0.418	0.65
06/06/2013	33.2	6.85	152.5	76.8	0.7	0	23.9	0	0	13	8.9	9.6	95.97	80	97.53	51.845	0.364	0.49
09/06/2013	11.6	5.4	20.97	10.53	0	1	24.8	0	2	2.3	1.2	2.4	25.99	24	29.26	17.477	0.396	0
12/06/2013	11.2	6	40.01	20	0	3	24.9	1	2	2.8	1.6	1.6	62.39	24	29.26	54.368	0.014	1.1
20/06/2013	9	6.5	90.39	45.19	0.1	2	24.6	2	6	7	3.3	4.81	45.09	48	58.52	34.951	0.155	0
05/09/2013	28	6.6	49.76	24.87	0.2	11	25	5	30	7.9	4.9	1.6	21.69	24	29.26	10.68	0.259	0.31
22/09/2013	4.8	6.4	100.8	50.4	0.1	4	23.9	2	8	15.7	11.2	2.4	17.99	48	58.52	41.748	0.162	0.42
23/09/2013	3.4	6.5	173.6	86.83	0.2	1	24.8	0	2	17.5	13.6	2.89	20.69	104	126.79	24.272	0.007	0.26
24/09/2013	4.3	6.7	57.85	28.98	0.3	0	24.9	0	4	8.7	6.5	1.6	17.89	32	39.01	40.777	0.36	0.66
26/09/2013	5.4	6.4	58.1	29.03	0.1	1	24.9	1	3	12.6	7	2.4	19.37	32	39.01	15.534	0.162	1.05
28/09/2013	30.3	6.2	16.38	8.19	0.1	2	24.7	2	2	3.5	2	2.4	23.19	16	19.51	15.534	0.31	0.58
21/10/2013	51.3	6.1	54.05	27.04	0	14	23.8	8	32	7.8	6.4	1.6	53.19	32	39.01	11.65	0.151	0.95
24/10/2013	17.3	6.4	35.5	17.75	0.1	2	24.8	1	8	4.2	2.7	1.6	18.89	24	29.26	33.009	0.094	0.75
25/10/2013	18.1	6.4	34.08	17.05	0.1	1	23.8	0	0	4.2	3.6	1.6	25.99	40	48.77	68.932	0.058	0.53
26/10/2013	13.2	6.3	38.13	19.07	0.1	0	23.9	0	0	2.8	0.5	1.6	17.99	40	48.77	14.563	0.299	0
29/10/2013	13.8	6.3	38.74	19.37	0.1	1	24.2	1	4	4.3	1.3	1.6	45.09	32	39.01	47.573	0.252	0.97
31/10/2013	5.1	6.1	20.24	10.12	0	2	24.6	1	5	3.4	0.8	1.6	19.29	24	29.26	14.563	0.249	0.65

Apendix C. Physico-chemical paramerts of rainwater at Amedzofe

DATE	Rainfall Amount	pH	EC	TDS	SAL.	TSS	Temp.	TURB.	Colour	Na$^+$	K$^+$	Ca^{2+}	Cl$^-$	OH$^-$	HCO$_3^-$	SO$_4^{2-}$	NO$_3^-$	Mg^{2+}
20/02/2013	7.2	4.89	50.3	25.2	0	2	24.9	0	0	3.5	2.4	3.52	5.19	20	24.38	12.04	0.274	0.09
21/02/2013	51.7	5.24	8.48	4.2	0	0	25	0	0	1	0.2	3.52	6.19	20	24.38	7.282	0.256	0.08
24/02/2013	7	5.39	14.1	7.1	0	1	24.9	0	0	0.9	0.3	3.2	1.19	10	12.19	13.3	0.732	0.06
02/03/2013	21.6	5.88	40.6	20.3	0	2	24.9	0	0	3.6	2.6	1.6	5.99	10	12.19	1.359	0.249	0.06
04/03/2013	33.4	5.3	11.09	5.5	0	1	25	0	0	0.8	0.4	2.88	2.39	10	12.19	8.155	0.195	0.08
10/03/2013	34.5	5.79	12.02	6	0	0	25	0	0	0.4	0.1	1.28	6.39	20	24.38	-3.98	0.047	0.08
26/03/2013	13.4	5.07	16.67	8.3	0	2	25	0	0	0.6	0.2	1.6	8.39	10	12.19	-1.17	0.249	0.98
30/03/2013	8.5	4.87	23	11.5	0	1	24.8	0	0	1.1	0.6	0.96	4.99	10	12.19	0.388	0.497	0.87
01/04/2013	16.5	5.2	3.43	1.7	0	2	24.9	0	0	0.1	0	2.24	10.99	10	12.19	4.563	0.339	0.13
08/04/2013	13.8	5.45	18.37	9.2	0	1	24.9	0	6	0.6	0.3	1.6	8.39	10	12.19	11.26	0.133	0.23
13/04/2013	7.1	4.89	24	12.1	0	2	24.7	0	10	0	0.2	1.6	6.99	10	12.19	4.854	0.166	0.14
18/04/2013	21.2	5.04	7.56	3.8	0	2	24.8	0	0	0.3	0.1	1.6	9.49	10	12.19	-1.85	0	0.06
21/04/2013	36.4	4.94	4.32	2.2	0	3	24.8	0	0	0	0	1.6	9.99	20	24.38	5.825	0.086	0.08
22/04/2013	14.9	5.05	4.83	2.4	0	1	24.7	0	0	0	0	1.92	11.99	10	12.19	4.272	0.108	0.08
25/04/2013	27.8	5.09	2.43	1.2	0	0	24.7	0	0	0	0	2.24	8.99	10	12.19	-0.87	0	0.38
30/04/2013	31.5	5.09	8.87	4.4	0	1	24.8	0	0	0	0.1	1.92	9.99	10	12.19	-0.29	0.263	0.09
09/05/2013	15.3	5.41	6.96	3.5	0	0	24.7	0	0	0.1	0	1.92	8.39	10	12.19	0.874	0.032	0.09
10/05/2013	43.2	5.56	5.71	2.9	0	1	24.9	0	0	0	0	1.92	6.79	20	24.38	-1.94	0.357	0.07
17/05/2013	6.3	5.55	18.48	9.2	0	0	24.7	0	0	0	0.2	1.28	5.99	10	12.19	12.14	0.076	0.12
18/05/2013	11.5	5.28	7.62	3.8	0	1	24.7	0	0	0	0	0.96	7.39	10	12.19	13.2	0.249	0.1
22/05/2013	8.4	5.41	12.36	6.2	0	1	24.8	0	0	0	0.2	1.92	5.99	10	12.19	3.398	0.259	0.12
29/05/2013	27.2	5.38	4.29	2.1	0	1	24.8	0	0	0	0	2.56	9.99	10	12.19	4.66	0.119	0.09
30/05/2013	22.7	5.82	2.71	1.4	0	1	24.7	0	0	0	0	3.52	7.99	10	12.19	9.708	0	0.33
01/06/2013	22.3	5.4	8.98	4.5	0	1	24.9	0	0	0	0.2	1.28	15.99	10	12.19	13.3	0.054	0.45
05/06/2013	8	5.41	6.41	3.2	0	2	24.9	0	0	0	0	1.6	7.99	10	12.19	6.505	0	0.34

08/06/2013	5.4	5.64	9.51	4.8	0	0	24.7	0	0	0	0	2.24	17.99	10	12.19	11.55	0	0.08
29/06/2013	72	5.71	11.8	5.9	0	4	24.8	0	0	0	0	2.56	7.99	10	12.19	4.078	0.36	0.12
02/07/2013	9.2	5.42	9.68	4.8	0	2	24.8	0	0	0	0	1.6	6.79	10	12.19	9.32	0.169	0.09
04/07/2013	28.6	5.27	8.87	4.4	0	2	24.8	0	0	0	0.3	1.6	11.19	10	12.19	2.621	0.198	0.4
08/07/2013	21.7	5.08	28	14	0	5	24.9	3	0	1.3	0.4	1.92	10.19	10	12.19	10.29	0.259	0.38
10/07/2013	42.8	5.59	7.18	3.6	0	2	24.9	1	0	0	0	1.28	15.99	10	12.19	11.46	0.342	0.42
11/07/2013	31.4	4.78	6.77	3.4	0	3	24.8	2	0	0	0	2.24	15.99	10	12.19	21.36	0.144	0.43
12/07/2013	44.2	4.77	3.87	1.9	0	2	24.7	3	0	0	0	2.24	6.99	10	12.19	5.339	0.328	0.48
14/07/2013	24.6	5.57	5.51	2.8	0	3	24.7	1	0	0	0	2.24	4.99	10	12.19	2.33	0.086	0.62
18/07/2013	19.3	5.16	5.45	2.7	0	1	24.6	1	0	0	0	2.56	4.99	10	12.19	12.82	0.321	0.55
22/07/2013	16.4	5.09	41.8	20.9	0	1	24.9	1	0	5.6	0.3	1.6	5.99	10	12.19	16.6	0.443	0.52
28/08/2013	15.3	6.2	6.28	3.14	0	2	23.9	0	0	1.3	0.6	1.6	6.59	16	19.51	6.214	0.115	0
30/08/2013	7.3	6.3	10.86	5.44	0	1	24.5	0	0	1.1	1	0.8	8.19	16	19.51	1.845	0.505	0
08/09/2013	65.2	5.9	3.85	1.93	0	0	24.6	0	0	0.9	0	0.8	7.99	16	19.51	2.718	0.314	0
09/09/2013	4.2	4.3	43.38	21.68	0.1	0	24.2	0	0	1.7	0.3	0.8	5.09	16	19.51	12.3	0.126	0.02
10/09/2013	8.2	5.6	4.11	2.06	0	0	24.4	0	0	1.2	0.1	0.8	4.39	16	19.51	5.631	0.112	0.11
14/09/2013	9.4	5.4	11.39	5.69	0	3	24.7	0	0	1.9	0	2.4	5.39	16	19.51	1.553	0.115	0.31
19/09/2013	55.3	5.7	3.92	1.96	0	2	23.8	0	0	3.1	1.2	1.6	10.19	24	29.26	3.786	0.67	0.02
20/09/2013	7.6	5.6	11.94	5.97	0	1	24.5	0	0	2	0	2.4	11.29	8	9.75	4.854	0.029	0.37
21/09/2013	21.3	5.8	20.16	10.08	0	2	23.8	0	0	4.3	0.4	1.6	4.99	16	19.51	1.748	0.259	0.06
02/10/2013	18.4	5.9	4.14	2.07	0	2	24	2	0	1.1	0	1.6	7.29	16	19.51	1.748	0.432	0.25
03/10/2013	44.3	5.4	7.94	3.97	0	0	24.2	0	0	1.1	0	1.6	5.69	8	9.75	15.53	0.324	0.07
08/10/2013	56.4	5.5	3.62	1.81	0	2	24.8	0	0	1	0	2.4	4.99	16	19.51	2.913	0.162	0
10/10/2013	12.5	5.2	3.87	1.94	0	1	24.6	1	0	1.1	0	1.6	10.29	16	19.51	8.252	0.112	0.31
15/10/2013	5.4	5.5	10.08	5.04	0	3	24.6	0	0	2.2	0	1.6	6.39	16	19.51	5.728	0.314	0
16/10/2013	14.4	5.7	3.54	1.77	0	1	24.2	0	0	1.1	0	1.6	5.29	16	19.51	2.233	0.735	0.09

Appendix D. Physico-chemical parameters of groundwater at Amedzofe, Kpando and Akatsi

ID	Sample type	pH	EC	TDS	SAL	Eh	Elevation	TEMP	Na^+	K^+	Ca^{2+}	Cl^-	OH^-	HCO_3^-	SO_4^{2-}	NO_3^-	Mg^{2+}
AS 1	Spring	6.67	339	170	0.1	11	199	28.2	44.4	6.1	3.53	25.99	224	273.1	10.39	0.187	0.93
AS 2	Spring	6.7	822	408	0.3	8.5	247	29.9	110.7	25.1	2.4	117.96	280	341.37	21.55	0.541	1.33
AS 3	Spring	6.24	49.1	25	0	40.6	523	25.4	16.3	0.1	4.01	13.99	40	48.77	9.81	0.299	0.78
AS 4	Spring	6.53	326	164	0.1	19.32	698	25.1	60.5	60.2	4.01	57.98	40	48.77	10.29	0.378	0.59
AS 5	Spring	5.41	257	129	0	84.9	682	23.6	54.9	52.7	2.4	17.99	40	48.77	12.04	0.959	0.11
AS 6	Spring	5.63	44.9	23	0	77.9	737	23.1	14.6	1.5	15.23	13.99	32	39.01	15.63	0.072	0.09
AS 7	Spring	5.07	47.7	24	0	105.3	723	24.1	12.7	1.7	2.4	14.59	24	29.26	55.34	0.537	0.23
AS 8	Spring	6.94	528	264	0.2	5.9	276	28.2	65.8	13.8	8.82	41.99	296	360.88	15.44	0.029	0.07
AS 9	Spring	5.43	108.4	54	0	84.2	454	26.3	25.2	33.4	4.01	45.99	32	39.01	19.13	0.191	0.47
AB 1	Borehole	6.37	480	240	0.2	86.7	46	30	282	6	4081	81.97	112	136.55	14.76	0.202	0.68
AB 2	Borehole	5.13	375	186	0.1	101.6	47	30.3	103.4	2.2	15.23	137.96	48	58.52	7.28	1.049	0.51
AB 3	Borehole	5.39	353	178	0.1	86	45	30.6	100.8	2.1	16.83	136.99	64	78.03	19.13	0.443	0.99
AB 4	Borehole	6.36	103	5.5	0.5	28.6	29	30.6	292	50	15.23	173.95	168	204.82	50.68	0.667	0.78
AB 5	Borehole	6.1	656	327	0.3	44.4	34	30.4	108.7	2	17.64	173.95	168	204.82	50.49	0.717	1.07
AB 6	Borehole	5.63	726	363	0.3	72.2	31	31.4	237	9	12.02	165.59	64	78.03	48.25	0.173	1.21
KB 1	Borehole	6.94	1163	581	0.5	5.2	112	29.6	360.9	7	11.22	73.98	496	604.71	47.77	0.649	0.93
KB 2	Borehole	5.95	1125	563	0.5	54.7	108	30.1	221	3	24.05	72.99	304	370.63	49.71	1.049	0.58
KB 3	Borehole	6.01	318	159	0.1	44.9	171	29.8	96	4	5.61	56.69	120	146.3	1.55	0.339	1.19
KB 4	Borehole	6.02	568	284	0.2	49.1	163	29.2	102	8.8	11.22	45.99	336	409.65	11.75	0.108	1.13
KB 5	Borehole	6.64	557	279	0.2	12.4	158	29.1	102.3	8	8.02	25.99	336	409.65	1.65	0.227	1.11
KB 6	Borehole	6.94	370	185	0.1	-5.8	158	31.4	94.2	36.4	4.81	61.98	104	126.79	11.75	0.195	0.37

Appendix E. Rainfall amount and δ ^{18}O and δ ^{2}H at Kpando.

DATE	Rainfall amount (mm)	δ^{18}O‰	δ^{2}H‰
21/02/2013	7.20	-0.41	6.61
25/02/2013	32.70	-3.85	-15.34
13/03/2013	4.70	0.08	16.35
15/03/2013	3.30	-0.39	8.99
20/03/2013	6.20	-0.22	10.70
21/03/2013	14.70	-0.50	9.27
31/03/2013	7.20	-0.46	3.14
09/04/2013	3.40	0.60	9.64
13/04/2013	2.30	0.83	13.65
25/04/2013	19.70	-3.93	-22.58
01/05/2013	6.40	-1.55	2.64
03/05/2013	2.20	-1.77	1.31
08/05/2013	12.70	-3.51	-17.01
10/05/2013	10.80	-3.26	-12.10
17/05/2013	9.40	-4.91	-27.27
18/05/2013	71.80	-5.52	-28.57
22/05/2013	40.90	-3.84	-17.24
28/05/2013	16.80	-3.28	-15.61
30/05/2013	10.40	-4.76	-22.30
01/06/2013	34.60	-3.75	-14.75
02/06/2013	4.90	-1.92	-6.31
08/06/2013	18.30	-3.85	-16.62
02/07/2013	15.30	-2.97	-16.10
04/07/2013	10.90	-0.66	5.30
09/07/2013	11.40	-1.13	4.43
14/07/2013	15.90	-2.65	-9.84
08/09/2013	24.20	-4.65	-27.36
09/09/2013	11.30	-4.61	-25.91
10/09/2013	3.30	-1.71	2.44
21/09/2013	12.80	-0.61	3.00
22/09/2013	8.80	-1.35	-4.15
03/10/2013	42.60	-5.08	-27.02
04/10/2013	24.40	-4.77	-24.24
06/10/2013	31.10	-4.42	-29.57
13/10/2013	26.80	-4.92	-25.23

Appendix F. Rainfall amount and δ ^{18}O and δ ^{2}H at Akatsi

DATE	Rainfall Amount (mm)	δ^{18}O‰	δ^{2}H‰
05/03/2013	41.50	-2.24	-10.45
26/04/2013	45.10	-0.96	4.18
30/04/2013	37.70	-2.68	-12.89
11/05/2013	34.80	-2.34	-11.4
22/05/2013	22.10	-2.22	-10.45
26/05/2013	83.00	-5.57	-30.16
30/05/2013	32.60	-1.31	-4.1
06/06/2013	33.20	-3.37	-14.68
09/06/2013	11.60	-2.79	-9.97
12/06/2013	11.20	-1.23	-1.15
20/06/2013	9.00	-0.29	3.80
05/09/2013	28.00	-1.87	-7.66
22/09/2013	4.80	0.26	7.12
23/09/2013	3.40	-0.94	5.18
24/09/2013	4.30	-0.76	6.69
26/09/2013	5.40	-0.70	4.58
28/09/2013	30.30	-3.65	-22.92
21/10/2013	51.30	-4.28	-21.14
24/10/2013	17.30	-0.25	4.55
25/10/2013	18.10	-0.43	3.57
26/10/2013	13.20	-1.64	-5.49
29/10/2013	13.80	-1.50	-4.23
31/10/2013	5.10	-1.19	1.39

Appendix G. Rainfall amount and δ ^{18}O and δ ^{2}H at Amedzofe

DATE	Rainfall amount (mm)	δ^{18}O‰	δ^{2}H‰
20/02/2013	7.20	-1.68	-6.40
21/02/2013	51.70	-6.24	-38.26
24/02/2013	7.00	2.73	14.72
02/03/2013	21.60	-2.51	-7.15
04/03/2013	33.40	-2.63	-9.02
10/03/2013	34.50	-1.79	-2.31
26/03/2013	13.40	-2.32	-12.87
30/03/2013	8.50	-3.17	-12.94
01/04/2013	16.50	-1.55	-4.18
08/04/2013	13.80	-4.24	-25.55
13/04/2013	7.10	-1.26	-2.44
18/04/2013	21.20	-3.71	-18.27
21/04/2013	36.40	-3.86	-22.95
22/04/2013	14.90	-4.24	-26.86
25/04/2013	27.80	-3.44	-14.20
30/04/2013	31.50	-4.16	-26.94
09/05/2013	15.30	-2.13	-6.08
10/05/2013	43.20	-4.76	-28.68
17/05/2013	6.30	-1.20	-1.26
18/05/2013	11.50	-3.07	-23.36
22/05/2013	8.40	-3.16	-8.39
29/05/2013	27.20	-4.31	-22.51
30/05/2013	22.70	-5.37	-29.45
01/06/2013	22.30	-1.74	-8.08
05/06/2013	8.00	-0.89	6.41
08/06/2013	5.40	-1.01	2.57
29/06/2013	72.00	-6.54	-38.51
02/07/2013	9.20	-1.81	-8.66
04/07/2013	28.60	-1.28	0.52
08/07/2013	21.70	-3.15	-19.69
10/07/2013	42.80	-4.60	-23.70
11/07/2013	31.40	-4.19	-24.93
12/07/2013	44.20	-5.25	-35.38
14/07/2013	24.60	-2.75	-11.39
18/07/2013	19.30	-4.93	-26.41
22/07/2013	16.40	-3.33	-14.02
28/08/2013	15.30	-2.74	-4.97
30/08/2013	7.30	-2.78	-3.62
08/09/2013	65.20	-5.67	-41.38
09/09/2013	4.20	1.00	11.45
10/09/2013	8.20	-3.74	-17.95

14/09/2013	9.4	-2.81	-17.39
19/09/2013	55.3	-5.11	-30.50
20/09/2013	7.6	-0.20	9.38
21/09/2013	21.3	-2.55	-2.74
02/10/2013	18.4	-2.29	-5.93
03/10/2013	44.3	-3.71	-15.68
08/10/2013	56.4	-4.29	-27.30
10/10/2013	12.5	-0.75	1.6
15/10/2013	5.4	-0.96	-1.36
16/10/2013	14.4	-3.63	-21.55

Apendix H. δ^{18}O‰ and δ^{2}H‰ in groundwater in Akatsi, Amedzofe and Kpando

Samples	Sample type	Elevation	δ^{18}O‰	δ^{2}H‰
AS 1	Spring	199	-2.63	-10.86
AS 2	Spring	247	-2.03	-8.27
AS 3	Spring	523	-3.40	-10.65
AS 4	Spring	698	-3.21	-11.21
AS 5	Spring	682	-3.13	-12.27
AS 6	Spring	737	-3.66	-13.89
AS 7	Spring	723	-3.17	-10.27
AS 8	Spring	276	-2.64	-8.02
AS 9	Spring	454	-3.38	-12.29
AB 1	Borehole	46	-3.24	-16.33
AB 2	Borehole	47	-3.59	-15.84
AB 3	Borehole	45	-3.41	-15.19
AB 4	Borehole	29	-3.43	-16.47
AB 5	Borehole	34	-3.46	-16.27
AB 6	Borehole	31	-3.43	-16.28
KB 1	Borehole	112	-2.70	-9.33
KB 2	Borehole	108	-2.30	-6.76
KB 3	Borehole	171	-2.78	-7.04
KB 4	Borehole	163	-3.14	-10.25
KB 5	Borehole	158	-3.06	-9.55
KB 6	Borehole	158	-2.07	-6.53

Appendix I: $\delta^{18}O$ and $\delta^{2}H$ standard reference material

Standards	**δD‰ vs VSMOW**		**$\delta^{18}O$ ‰ vs VSMOW**	
	This work	Certified value	This work	Certified value
LS 2	-68.7	-68.78	-9.65	-9.6
LS 1	+2.15	+2.1	+0.16	+0.24
LS 3	-43.75	-43.67	-7.21	-7.56