UNIVERSITY OF CAPE COAST

# HYDROCHEMISTRY OF THE AYENSU RIVER BASIN IN THE CENTRAL REGION OF GHANA

BY

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# DECLARATION

Candidates Declaration

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

Candidate's signature:............................ Date: 10/8/16

Name: CHRISTIAN KWADZO AVI

Supervisors' Declaration

We hereby declare that the preparation and presentation of the thesis were supervised in accordance with guidelines on supervision of thesis laid down by the University of Cape Coast.

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# ABSTRACT

The focus of this work was to use the hydrochemical and isotopic composition of groundwater and surface water resources to establish the hydrochemistry, recharge mechanism, and interrelationship between surface and groundwater resources in the Ayensu River Basin. The methodology consisted of sampling and laboratory analysis of both groundwater and surface water resources. $Na^+$ and $K^+$ were determined using flame photometer, $Ca^{2+}$ and $Mg^{2+}$ by EDTA titration and the trace metals were determined using atomic absorption spectrometer. The anions were analysed using Dionex ICX- 90 Ion Chromatography system. Analysis of the hydrochemical survey data from the study area revealed that the groundwater is mildly acidic (4.77 - 7.8). Four boreholes at Gyangyanadze, Brahabekume, Topiase and Aduafokwa had their Total Dissolved Solids (TDS) values above 1000mg/L. Three major water types have been delineated using the phase diagrams. These are Na - Cl, Ca - Mg - Cl and Ca - Mg - $SO_4^{2-}$ waters. Chloride ion ($Cl^-$) concentrations of 10 boreholes exceeded the permissible levels of 250mg/L for $Cl^-$ ion and 7% of the groundwater samples had their $NO_3^-$ concentrations exceeding the WHO limit. Approximately 43% and 57% of the samples had the $Al^{3+}$ and $Fe^{2+}$ concentrations respectively, above the WHO maximum acceptable limits and 25% of the water samples had their $Cd^{2+}$ concentration above the WHO limit. The groundwater chemistry is controlled mainly by rock weathering and to a very small extent by evaporation during both the dry and rainy seasons. From the stable isotope data for deuterium ($\delta^2H$ ‰) and Oxygen - 18 ($\delta^{18}O$ ‰) it is concluded that recharge to the aquifer system in the Ayensu River Basin mainly come from local rainfall.

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# DEDICATION

This work is dedicated in memory of my father, Ex-Sgt Kwadzo Avi.

## TABLE OF CONTENTS

## LIST OF TABLES

## LIST OF FIGURES

# CHAPTER ONE

# INTRODUCTION

## BACKGROUND

The availability of freshwater is one of the greatest issues facing mankind today. Problems associated with freshwater availability affect the lives of millions of people. It has consequently attracted a wide scale international attention viz UN Agencies and related international/regional, governmental and non-governmental organizations. The rapid growth of population coupled with the steady increase in the demand for water for agricultural and industrial activities have imposed severe stress on the available freshwater resources in terms of both the quantity and quality. This requires a consistent and careful assessment and management of water resources for sustainable development (Mook, 2000).

Modern developments and population growth have increased demands for water globally. Thus, the welfare of every society is tied to the sustainable exploitation of water and its resources (Bear, 2000). Much more water cannot be acquired without a continual expansion of hydrological research. In this respect, the development of practical implementation of isotope methodologies in water resources assessment and management has been part of the International Atomic Energy Agency's (IAEA) programme in nuclear applications. Isotope studies applied to a wide spectrum of hydrological problems related to both surface and ground water resources and studies in hydro-ecological systems is presently an established scientific discipline, often referred to as "Isotope Hydrology" (Mook, 2000).

Analysing and interpreting the chemistry of water can provide valuable insights into groundwater-surface water interactions. Dissolved constituents can be used as environmental tracers for tracking the movement of water. For example, a particular characteristic of the groundwater chemistry can be used as an indicator of groundwater- surface water interactions, when measured in the surface water medium. Such tracers can be used to determine source areas of water and dissolved chemicals in catchments, calculate hydrologic and chemical fluxes between groundwater and surface water, calculate water ages that indicate the length of time water and dissolved chemicals have been present in the catchment (residence times), and determine average rates of chemical reactions that take place during transport (Winter *et al*, 1998).

The possibility of seawater intrusion, quality changes due to vertical leakage and other ill effects of over exploitation are anticipated in the Ayensu River Basin. Environmental chemical isotopes ($^{2}H$, $^{18}O$, $^{13}C$, $^{14}C$), hydro-chemistry (major-ions) and in-situ physico-chemical parameter (conductivity, Temperature, pH, etc) would be used to investigate the recharge processes. The isotopic composition of the groundwater and dissolved compounds are relevant to understanding the water's geochemical history and the hydrological condition of the system. Hence, stable isotope values of oxygen and deuterium will help as important indicators for the origin of the water.

## STATEMENT OF THE PROBLEM AND JUSTIFICATION

In the Ayensu River Basin, groundwater is the principal and sometimes the only source of potable water supply. It is in line with this that the Government and Non-governmental bodies put so much emphasis and funds into the provision of boreholes and lined dug wells mainly for domestic water supply. It has been observed that some of the boreholes dry out and others develop quality problems a few years after construction. Thus, making the boreholes unavailable for water supply. In other words, the purpose for which the boreholes have been drilled is being defeated. Therefore, inspite of the importance of groundwater for the socio-economic development of Ayensu Basin, studies that can provide the basic data and information on which the present and future water quantity and quality assessment can be based have not been carried out. The processes responsible for the evolution of the quality of groundwater in the basin are also unknown. It is, therefore, extremely difficult if not impossible to predict the quality of water and recharge mechanism in the basin. This study, which involves the use of hydrochemical and isotopic data of the groundwater, will help characterize the aquifers into water types, establish major cations and anions data bank, chemical processes responsible for water quality, provide understanding to the recharge mechanism, and the possible interactions between surface and groundwater resources and generally the groundwater flow mechanism in the Basin. The study will thus be beneficial to the water supply industry for better management and utilization of the water resources on sustainable basis to meet future challenges.

## OBJECTIVE OF RESEARCH

The main aim of this project is to use the hydrochemical and isotopic composition of groundwater and surface water resources to establish the hydrochemistry, recharge mechanism, and interrelationship between surface and groundwater resources in the Ayensu River Basin.

The specific objectives are:

- to establish the hydrochemical facies in groundwater in the river basin.
- to evaluate the availability, suitability and movement of groundwater resources in the area to determine the chemical processes responsible for evolution of groundwater quality in the basin

# CHAPTER TWO

## LITERATURE REVIEW

### HYDROCHEMISTRY

Hydrochemistry is a useful integrator of major biological, chemical and physical processes in small catchments. It is the output, that couples hydrology to terrestrial processes, including plant decomposition, soil cation exchange, chemical weathering, biological uptake and mineralization. Because small catchments are sensitive indicators of changes in ecosystems due to human activities, they should be used as early warning systems of ecological change. Hydrochemical catchment studies as investigations focus on the chemical composition of the runoff and the processes in the terrestrial and aquatic environments controlling this composition.

The hydrochemical response represents an integration of hydrological, chemical, physical and biological reactions within catchment ecosystems. Of specific interest are the changes in hydrochemistry caused by anthropogenic factors, such as; acidic deposition, land-use changes and climatic change. Small catchments may serve as early warning systems of ecological change because they are located at the headwaters or uplands of larger drainage areas; they are physically well-defined allowing for the construction of accurate element balances and are sensitive to disturbances (Gibson *et al*, 2005).

Groundwater quality appraisal is gaining importance, due to intense urbanisation, industrialization and agricultural activities putting the soil and groundwater to greater risk of contamination (Ackah *et al.*, 2011; Sayyed & Wagh, 2011; Tiwari, 2011). Water pollution also threats human health, economic development and social prosperity (Milovanovic, 2007). The chemical composition of groundwater is controlled by many factors, including the composition of the precipitation, geological structure, mineralogy of the watersheds, aquifers, geological, processes within the aquifer along with influence of external pollution agencies like effluents from agricultural return flow, industrial and domestic activities. An understanding of the geochemical evolution of groundwater is important for a sustainable development of water resources in the present state of art (Srinivasamoorthy, *et al*, 2012).

Demarcating the character of the groundwater in varied space, was proved to be an important technique in solving different geochemical problems (Chebotarev, 1955; Hem 1959; Back & Hanshaw, 1965; Srinivasamoorthy *et al.*, 2011). Calculation of minerals saturation index and thermodynamic equilibrium studies to decipher the possible reactant and product minerals (Garrels & Christ, 1965).

## Hydrology

Classical hydrology, may be defined a bit more precisely as the science of water on the continents, above, on, and below the surface. This especially means that it does not include the ocean, which is treated by the field of oceanography. Hydrology is a physical science, which deals with such issues as water (mass) balance and water fluxes, or generally the movement of water in space and time. The classical hydrological systems are catchments of rivers and aquifers, where quantities such as precipitation, recharge, storage, and discharge are determined. Hydrology is, to a large extent focussing on quantitative aspects, such as the study of river discharge (e.g. for flood prediction). However, it also has chemical, biological, and technical/sociological aspects. Some related aspects are dealt with by the engineering sciences, e.g. water supply, wastewater, flood protection, etc. Sub disciplines of hydrology or disciplines related to it are:

- Hydrogeology and soil physics (water in the saturated and unsaturated zones)
- Physical Oceanography and Limnology (water in the ocean and lakes/rivers)
- Meteorology and (palaeo)climatology (water in the atmosphere, precipitation)

The hydrosphere includes all forms of water on and below the surface of the Earth. This includes the ocean and all parts of the global water cycle except the atmospheric part (water vapour, precipitation). The global hydrological cycle is the framework in which the different aquatic systems exist. Table 1 lists the compartments of the hydrosphere. 70 % of the Earth's surface are covered by oceans, which contain 97 % of the water in the hydrosphere (including the cryosphere) (Aeschbach-Hertig, 2013).

Table 1: Compartments of the hydrosphere

| | Volume in $10^3$ km$^3$ | % of total freshwater | Flux $10^3$ km$^3$/year | turn-over time year |
|---|---|---|---|---|
| Salt water | | | | |
| Oceans | 1350 | | 425 | 3000$^{1}$) |
| Freshwater | | | | |
| Ice | 27 800 | 69.3 | 24 | 12 000$^{2}$) |
| Groundwater | 8 000$^{*}$ | 29.9 | 15 | 500$^{3}$) |
| Lakes | 220$^{**}$ | 0.55 | | |
| Soil moisture | 70 | 0.18 | 90 | 0.8$^{4}$) |
| Atmosphere | 15.5 | 0.038 | 496 | 0.03$^{5}$) |
| Reservoirs | 5 | 0.013 | | |
| Rivers | 2 | 0.005 | 40 | 0.05$^{6}$) |
| Biomass | 2 | 0.005 | | |
| Total | 40 114 | 100 | | |

Source:Mook(2001)

## The Hydrologic Cycle

The endless circulation of water as it moves in its various phases through the atmosphere, to the Earth, over and through the land, to the ocean, and back to the atmosphere is known as the hydrologic cycle. This cycle is powered by the Sun: through phase changes of water (i.e. evaporation and condensation) involving storage and release of latent heat, affects the global circulation of both the atmosphere and oceans, and hence is instrumental in shaping weather and climate. The efficiency of water as a solvent makes geochemistry an intimate part of the hydrologic cycle: all water-soluble elements follow this cycle at least partially. Thus, the hydrologic cycle is the integrating process for the fluxes of water, energy, and the chemical elements (Sophocleous, 2002).

A hydrologic cycle describes the continuous movement of water above, on, and below the surface of the Earth. The water on the Earth's surface (surface water) occurs as streams, lakes, and wetlands, as well as bays and oceans. Surface water also includes the solid forms of water-snow and ice. The water below the surface of the Earth primarily is ground water, but it also includes soil water (Winter *et al*, 1998). The hydrological cycle starts with evaporation from the oceans (Fig. 1), estimated at 425,000km$^3$ (1176 mm) per year. Rainfall over the oceans is estimated at 385,000km$^3$ (1066mm), leaving an excess of 40,000km$^3$ (equivalent to 110mm) of water as vapour, which is transported by atmospheric circulation (advection) to the continents. The main vapour flux travels from the warm equatorial to the cool high-latitude regions (Mook, 2000).

Precipitation, which is the source of virtually all freshwater in the hydrologic cycle, falls nearly everywhere, but its distribution is highly variable. Similarly, evaporation and transpiration return water to the atmosphere nearly everywhere, but evaporation and transpiration rates vary considerably according to climatic conditions. As a result, much of the precipitation never reaches the oceans as surface and subsurface runoff before the water is returned to the atmosphere. The relative magnitudes of the individual components of the hydrologic cycle, such as evapotranspiration, may differ significantly even at small scales, as between an agricultural field and a nearby woodland (Winter *et al*, 1998).

Precipitation is delivered to streams on the land surface as overland flow to tributary channels, and in the subsurface as interflow or lateral subsurface flow and base flow following infiltration into the soil. A portion of the infiltrated water enters the groundwater or aquifer system by passing through the unsaturated zone, and it exits to the atmosphere, surface water, or to plants. As shown in Fig. 2, the flowlines deliver groundwater from the highlands towards the valleys, or from the recharge areas to the discharge areas. The patterns of groundwater flow from the recharge to the discharge areas form groundwater flow systems, which constitute the framework for understanding recharge processes (Sophocleous, 2002). Fig. 2 illustrates different parts of the land-based portion of the hydrologic cycle that affect an individual watershed or catchment.

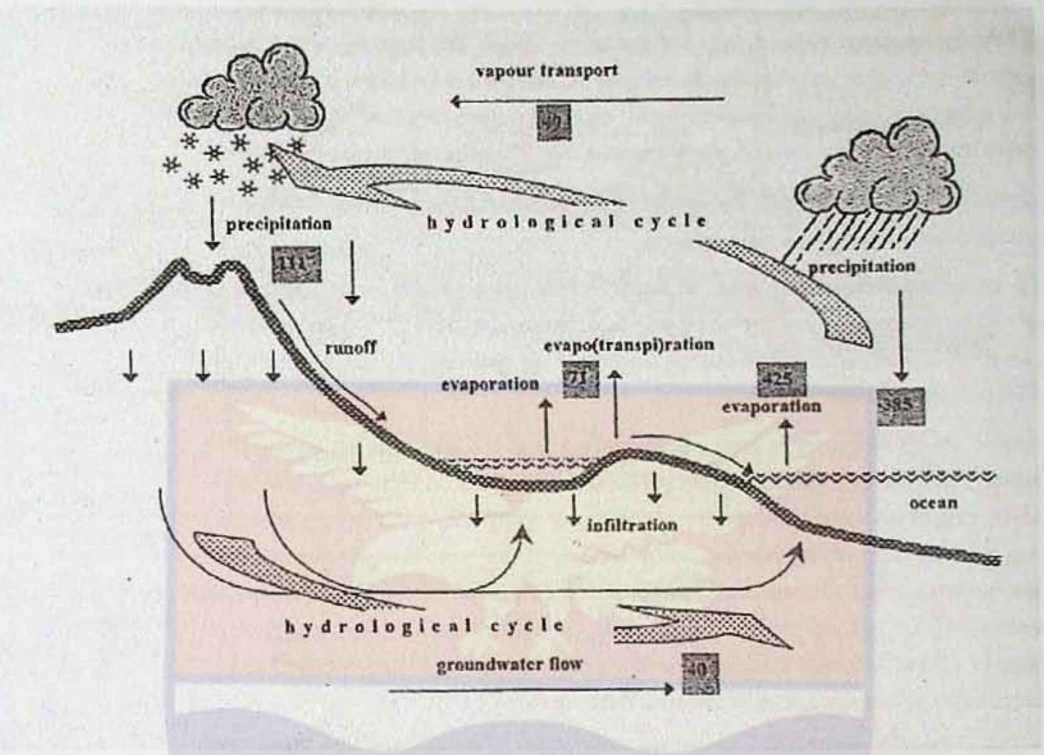


Figure 1: Schematic representation of the global hydrological cycle. The overall figures refer to the water fluxes in $10^3$ $km^3$ per year (Mook, 2000).

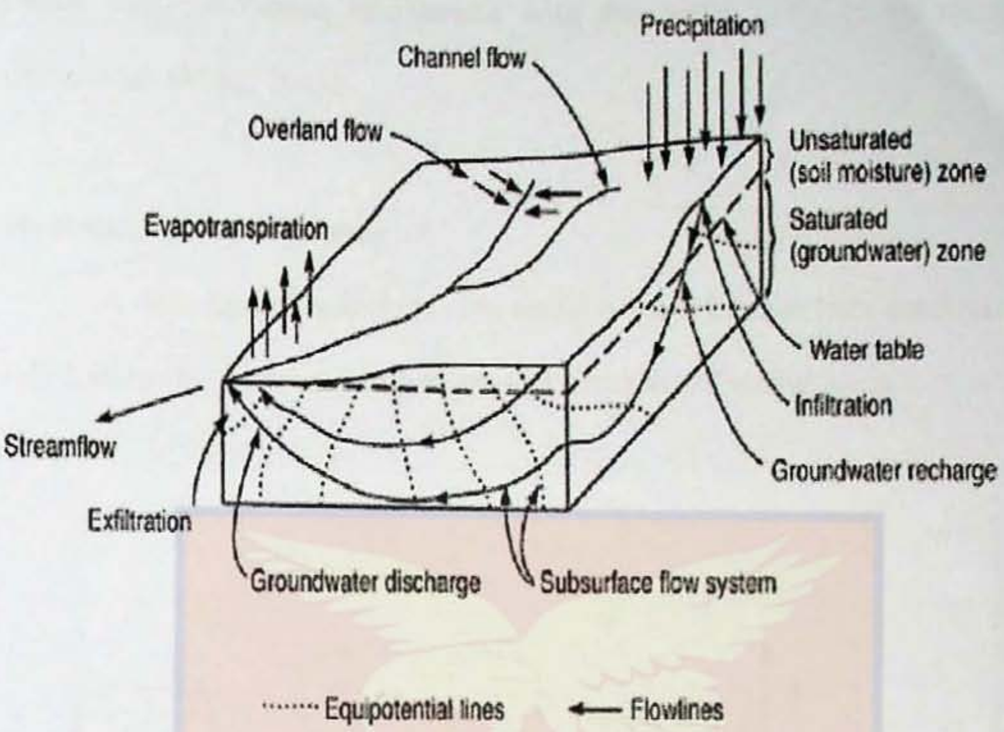


Figure 2: Schematic representation of the hydrologic cycle (Freeze, 1974)

The processes of interest for the hydrological water balance are precipitation, evaporation, evapotranspiration, surface discharge, and groundwater recharge (infiltration). Lakes and aquifers act as temporary storage reservoirs. The distribution of precipitation on Earth is very uneven. Tropical forests and coastal mountain ranges receive most precipitation. The subtropics and the inner regions of the large continents of the northern hemisphere are dry. Water scarcity prevails at the places where dry climate coincides with high (and often still increasing) population density (e.g. northern Africa, the Middle East, and northern China). Most of the water consumption goes into irrigation of fields to produce food. The worldwide demand for irrigation water is about 3'00 km3/yr, or nearly one fourth of the available renewable resource. This shows clearly that the human interference with the water cycle is substantial (Aeschbach-Hertig, 2013).

## Hydrological water balance

A basic tool of hydrology is to set up a water balance for a catchment. Fig. 3 shows the essential components and processes of a river basin.

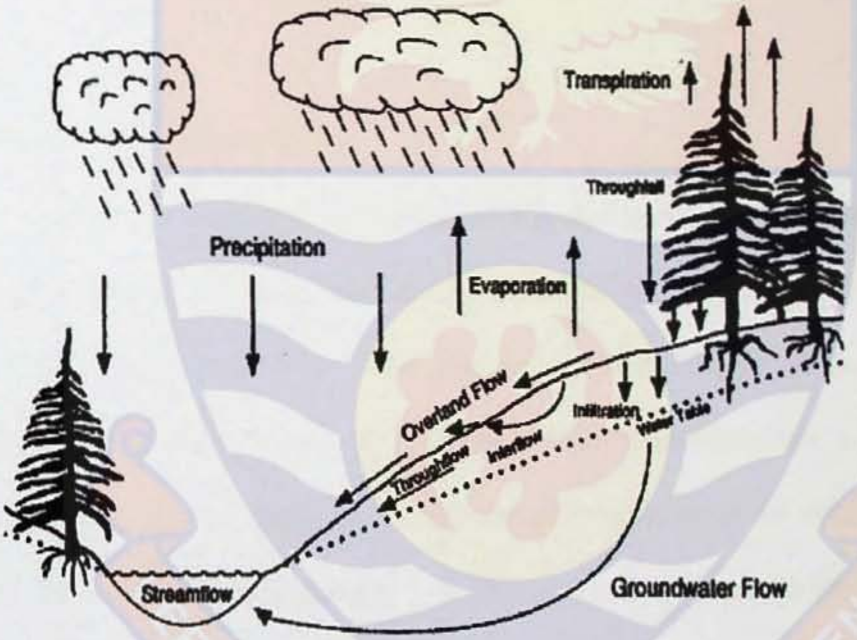


Figure 3: Components of the hydrological budget for a catchment (Mook, 2001).

Incoming precipitation reaches the river by direct overland flow or by several slower pathways through the subsurface. Output from the catchment happens only by evapo(trans)piration and by the river discharge (Aeschbach-Hertig, 2013). In a formal description, such a hydrological system may be seen simply as a reservoir with

- input P (precipitation)
- output R (runoff)
- output ET (evapotranspiration)

Mass conservation then requires that input – output equals the change in storage, which mathematically can be expressed as: (Aeschbach-Hertig, 2013).

$$\mathbf{P - R - ET} = \frac{dS}{dt}$$

**Groundwater (hydrogeology)**

Groundwater begins with precipitation that seeps into the ground. The amount of water that seeps into the ground will vary widely from place to place, depending on the slope of the land, amount and intensity of rainfall, and type of land surface. Porous, or permeable land, containing lots of sand or gravel will allow as much as 50 percent of precipitation to seep into the ground and become groundwater. In less permeable areas, as little as five percent may seep in. The rest becomes runoff or evaporates. Over half of the fresh water on Earth is stored as groundwater. As water seeps through permeable ground, it continues downward until it reaches a depth where water has filled all the porous areas in the soil or rock. This is known as the saturated zone. The top of the saturated zone is called the water table. The water table can rise or fall according to the season of the year and the amount of precipitation that occurs.

**Basics of hydrogeology**

By groundwater, we mean the water in the subsurface that completely fills the pore space in a soil or rock matrix. The uppermost zone of the subsurface, where the pore space is only partly filled with water, and the remainder contains air, is referred to as the vadose or unsaturated zone. This is the realm of soil physics. Hydrogeology and groundwater hydrology treat mainly the saturated zone. The zones in the subsurface are shown in Fig. 4. A geological formation that is filled with water and has a connected pore space in which the water can circulate relatively easily is called aquifer. If the formation is (nearly) impermeable for water, it is called aquitard. There are different types of porous media in which groundwater can circulate. The most important in practice are fine-grained sediments such as gravel, sand, and sandstone. The pores in such media are well-connected, and the system is relatively homogeneous. In hard rocks, such as granite, the water can only move in fractures ("fractured rock" aquifers). A third type of porous medium is karst, where water flows in relatively large openings or cavities. This occurs in limestone (calcite rock), which can be partly dissolved by the water. An important quantity to characterise porous media is the porosity, which is defined as: (Aeschbach-Hertg, 2013).

$$\theta = \frac{Vpores}{Vtotal}$$

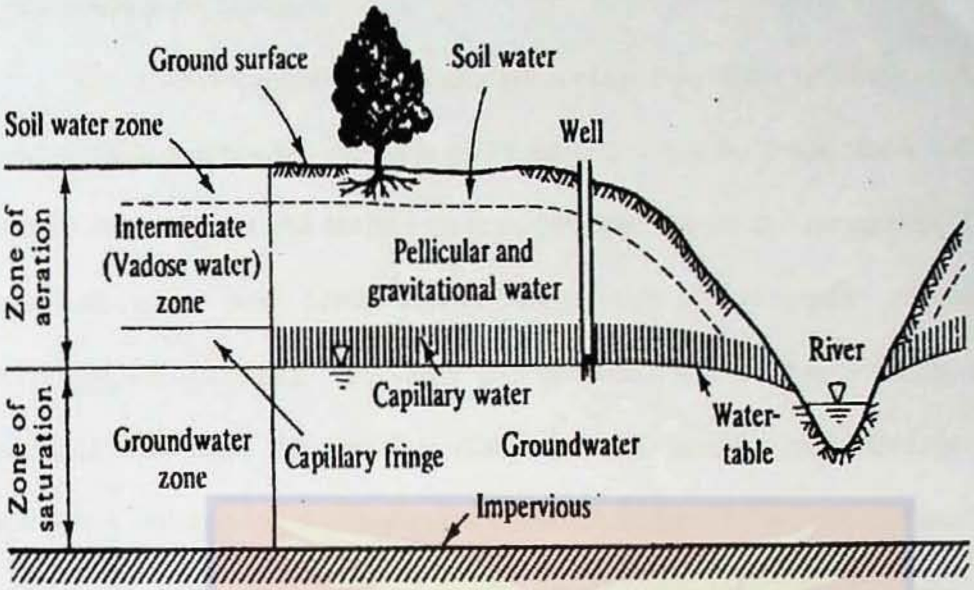


Figure 4: Zones in the subsurface (Bear, 1979).

The soil water zone includes the root zone. The water content is subject to strong daily and seasonal fluctuations. Depending on the ratio of infiltration and evaporation, the water moves downwards or upwards. In the vadose zone, immobile water is held by capillary forces. In the case of infiltration, the water moves downwards due to gravity. The capillary fringe extends from the water table of the saturated zone upwards up to the maximum capillary rise height. This height depends on the soil type and is small in coarse material but can reach up to 3 m in very fine material with small pores. The pressure in the capillary fringe is below the atmospheric pressure, as water is sucked up by capillary forces. The groundwater zone or saturated zone is the zone beneath the groundwater table. The groundwater table is defined as the level in the saturated zone where the hydrostatic pressure equals the atmospheric pressure.

## Groundwater recharge

Groundwater recharge normally takes place by diffuse infiltration. Part of the rainfall that reaches the earth will disappear again by evaporation, either directly from the wet soil surface or from interception on the vegetation. The remaining water may partly runoff along surface and partly infiltrate, recharging soil moisture. Soil water will percolate further downward to the saturated zone after the soil has reached a soil-specific concentration of moisture. Concentrated recharge takes place via water that has accumulated in depressions or streams in cases where the stream bed is above the groundwater table. Recharge relates to the water added to the groundwater system, that is, to the saturated zone. Thus, recharge is the balance between the amount of water that infiltrates into the ground and evapotranspiration losses. The location of recharge areas is of prime importance in modern hydrochemistry, as such these areas have to be protected in order to preserve groundwater quality. Urbanization, agriculture, and almost any other kind of human activity may spoil the quality of recharge water (Mook, 2000).

## Groundwater discharge

Groundwater discharge normally takes place by subsurface drainage to streams. The average turnover time of groundwater is determined by the total flux, of recharge, and the storage of the basin. The flow density however, normally decreases downward, so that the age of the water roughly increases logarithmically with deph. Water is stored during periods of high recharge: this results in a rise of the groundwater table and an increase of the hydraulic gradient, so that the discharge increases. Moreover, a rise of the groundwter table often means that the lower-order and less deeply incised stream branches are activated to take part in the drainage process, which can amplify the drainage rate by an order of magnitude. Saturation-excess overland flow through rills and gullies is the extreme condition which occurs when the groundwater table reaches the surface. Discharge, therefore, relates to the emergence of groundwater at the surface as springs, water feeding swamps and lakes, and water pumped from wells. Discharge is the output of groundwater (Mook, 2000).

A dry period reverses the process; groundwater is then released from storage because discharge exceeds recharge. Consequently the groundwater table drops, discharge decreases and stops when the water table at the divide has reached the level for the deepest incised channel and the hydraulic gradient has become zero. In arid areas where recharge is low and groundwater tables are deep, groundwater flow is more steady and fluctuations are dominated by long term cycles of drought and wet spells. Residence times of groundwater range between months for shallow drainage systems to thousands of years for deeper systems, and especially in arid areas with low recharge and large turnover time. Part of soil moisture and shallow groundwater is subsequently re-evaporated, mainly via transpiration by the vegetation. The excess of surface water as well as groundwater is eventually discharged by rivers and to a less extent by direct groundwater discharge into the sea (Mook, 2000).

**Evapotranspiration**

Only part of the water infiltrating into the ground keeps moving downward into the saturated groundwater zone. An important part of infiltrated water is transferred back into the atmosphere. Two major mechanisms are involved: evaporation and transpiration, together called evapotranspiration.

Evaporation is a physical process, caused by heat energy input, providing water molecules with kinetic energy that transfers them from an interpore liquid phase into a vapor phase. Evaporation depends on local temperature, humidity, wind, and other atmospheric parameters as well as soil properties. Water infiltrated into the ground is partially protected from evaporation. Evaporation occurs mainly from the uppermost soil surface, and when this is dry further evaporation depends on capillary ascent of water, which is a slow and only partially efficient process. It is then clear that the relative contribution of precipitation to recharge is proportional to the amount of rain falling in each rain event. Intensive rain events push water deep into the ground, contributing to recharge, whereas sporadic rains only wet the soil, and the water is then lost by subsequent evaporation (Mazor, 2004). The mode of rainfall and degree of evaporation influence groundwater composition. High degrees of evaporation result in enrichment of the heavier stable isotopes of hydrogen and oxygen and in higher concentrations of dissolved salts.

Transpiration is the process by which plants lose water, mainly from the surfaces of leaves. Plants act as pumps, their roots extracting water from the soil and the leaves transpiring it into the atmosphere.

Thus the depth of the transpiration effect on soil moisture is defined by the depth of a plant's root system.

Table 3: Annual water balance of continents and oceans

| | Area in $10^3$ km$^2$ | P $10^3$ km$^3$ | | E | | D | | D/P % |
|---|---|---|---|---|---|---|---|---|
| | | $10^3$km$^3$ | mm | $10^3$km$^3$ | mm | $10^3$km$^3$ | mm | |
| Europe | 10 | 6.6 | 657 | 3.8 | 375 | 2.8 | 282 | 43 |
| Asia | 44.1 | 30.7 | 696 | 18.5 | 420 | 12.2 | 276 | 40 |
| Africa | 29.8 | 20.7 | 696 | 17.3 | 582 | 3.4 | 114 | 16 |
| Australia | 8.9 | 7.1 | 803 | 4.7 | 534 | 2.4 | 296 | 33 |
| Id.w.o islands | 7.6 | 3.4 | 447 | 3.2 | 420 | 0.2 | 27 | 6 |
| N. America | 24.1 | 15.6 | 645 | 9.7 | 403 | 5.9 | 242 | 38 |
| S. America | 17.9 | 28.0 | 1564 | 16.9 | 946 | 11.1 | 618 | 40 |
| Antarctica | 14.1 | 2.4 | 170 | 0.4 | 28 | 2.0 | 142 | 83 |
| All Continents | 148.9 | 111 | 746 | 71.5 | 480 | 39.7 | 266 | 36 |
| Arctic Ocean | 8.5 | 0.8 | 97 | 0.4 | 53 | 0.4 | 44 | 45 |
| Atlantic Ocean | 98.0 | 74.6 | 761 | 111.1 | 1133 | -36.5 | -372 | -49 |
| Indian Ocean | 77.7 | 81 | 1043 | 11.5 | 1294 | -19.5 | -251 | -24 |
| Pacific Ocean | 176.9 | 228.5 | 1292 | 212.6 | 1202 | 15.9 | 90 | 7 |
| All oceans | 361.1 | 385 | 1066 | 224.7 | 1176 | -39.7 | -110 | -10 |

Source: Baumgartner and Reichel (1975).

[P = precipitation, E = evaporation, D = discharge]

Evapotranspiration returns distilled water into the atmosphere. The salts, dissolved in the original precipitation water, remain in the soil zone, and at the end of dry seasons some of these salts accumulate on the surface. The next rain event re-dissolves these salts, and eventually they are brought into the saturated zone. Thus recharge water is richer in atmospherically derived salts than the original precipitation ( Mazor, 2004).

## Natural Variations in the Composition of Groundwater

What gives groundwater its taste is the amount and type of dissolved minerals within it. Pure water, i.e., having no dissolved minerals, does not occur naturally. Factors that control the dissolved minerals in groundwater include:

(i) The types of minerals that make up the aquifer

Virtually all groundwater comes from precipitation that soaks into the soil and passes down to the aquifer. Rainwater has a slightly acidic pH, therefore it tends to dissolve solid minerals in the soil and in the aquifer. Different rocks, e.g., sandstone, limestone and basalt all have different minerals and therefore, groundwater in contact with these different geologic materials will have different compositions and therefore different tastes.

(ii) the length of time that the water is in contact with the minerals, (the residence time of the groundwater in the aquifer). The longer the groundwater is in contact with the minerals, the greater the extent of its reaction with those minerals and the higher will be the content of dissolved minerals.

(iii) the chemical state of the groundwater.

The chemical state of groundwater is usually defined in terms of pH, temperature and oxidation-reduction potential. These parameters control and are influenced by chemical reactions. As temperatures change seasonally, as the water table rises and falls, or as recharge rates vary, the chemical state will change and, as a result, so will the composition of groundwater.

Some of the constituents found in groundwater, however, are not abundant in common rocks and minerals, for example, chloride ($Cl^-$) and sulfate ($SO_4^{2-}$). The probable source for these chemicals is the infiltrating precipitation (Nelson, 2002).

The table below (Table 4) illustrates typical natural water compositions, from rainwater to seawater, groundwater in different aquifers, to groundwater that has been in contact with the aquifer for different periods of time.

Key to Analyses:

(1) Rainwater from Menlo Park, California;

{2 Average rainwater from sites in North Carolina and Virginia;

(3) Great Salt Lake, Utah;

(4) Average seawater;

(5) Groundwater from limestone of the Supai Formation, Grand Canyon;

(6) Groundwater from volcanic rocks, New Mexico;

(7) Groundwater from a spring, Sierra Nevada Mountains: short residence time;

(8) Groundwater from metamorphic rocks in Canada: long-residence time

Table 4: Examples of the composition of natural water from a variety of locations and environments (all concentrations in mg/L)

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Calcium | 0.8 | 0.65 | 241 | 400 | 144 | 6.5 | 3.11 | 4540 |
| Magnesium | 1.2 | 0.14 | 7200 | 1350 | 55 | 1.1 | 0.7 | 160 |
| Sodium | 9.4 | 0.56 | 83,600 | 10,500 | -27 | -37 | 3.03 | 2740 |
| Potassium | - | 0.11 | 4070 | 380 | -2 | -3 | 1.09 | 32.1 |
| Bicarbonate | 4 | - | 251 | 28 | 622 | 77 | 20 | 55 |
| Sulphate | 7.6 | 2.2 | 16400 | 185 | 60 | 15 | 1.0 | 1 |
| Chloride | 17 | 0.57 | 140,000 | 35,000 | 670 | 222 | 36 | 20,338 |
| Silica | 0.3 | - | 48 | 3 | 22 | 103 | 16.4 | 8.5 |
| TDS | 38 | 4.7 | 254,000 | 35,000 | 670 | 222 | 36 | 20,338 |
| pH | 5.5 | - | 7.4 | - | - | 6.7 | 6.2 | 6.5 |

Source: Nelson (2002).

[Sources of Analyses: Analyses 3, and 7 (Drever, 1982); Analyses 1, 2, 4, 5 and 6 (Hem, 1985); Analysis 8 (Frape *et al*, 1984). TDS is total dissolved solids.]

It is clear, then, why groundwater from different wells may taste different. The wells may be in different geologic units or of significantly different depths. Groundwater at greater depths (residence time from 10s to 1000s of years) usually has been in contact with the aquifer for much longer than shallow groundwater (residence time from months to 10s of years) (Heath, 1989).

Table 5: Natural substances that may reduce the aesthetic quality of groundwater

| **Characteristics or Symptoms** | **Cause(s)** |
|---|---|
| Hardness: Low suds production with soap, mineral scale developed in water heater and plumbing | High concentrations of calcium and magnesium |
| Color: Water has a color other than clear | Red/Brown: iron<br>Black: manganese or organic matter<br>Yellow: dissolved organic matter such as tannins |
| Taste: Metallic or mineral taste | Metallic: dissolved metals such as iron and manganese<br>Mineral taste: high concentration of common minerals such as sodium, chloride, sulfate, calcium, etc. |
| Odor: Musty or rotten egg smell | Musty: algae or bacterial growth in pipes or well<br>Rotten egg: hydrogen sulfide |
| Appearance: cloudy with or without color | Suspended mineral matter or microorganisms |

Source: Nelson (2002).

## Chemical State of Groundwater

The chemical state of groundwater is generally defined in terms of three parameters: the temperature, pH, and oxidation-reduction potential (redox potential). These factors are often influenced by chemical reactions between the groundwater and aquifer materials or mixing with different waters and these factors in turn control the chemical composition of Groundwater (Nelson, 2002).

### (a) Temperature.

The total dissolved solids (TDS) in groundwater, largely derived from aquifer minerals that dissolve in groundwater, will change significantly as a function of temperature and pH. At any given temperature, there is a specific concentration of a dissolved mineral's constituents in the groundwater that is in contact with that mineral. The actual concentration is temperature dependent, e.g., at higher temperatures, groundwater can dissolve more of the mineral. Even changes in groundwater temperature of only 5 to 10°C can cause detectable changes in TDS. For groundwater deeper than 15 to 30 metres, seasonal changes are generally less than one degree and temperature variations do not play a significant role in groundwater composition (Heath, 1989). For shallow groundwater, larger seasonal variations, related to warming of or cooling at the surface are common, and may be on the order of 5 to 10 degrees or more. Another source of temperature change in shallow groundwater, and occasionally deeper water, is the introduction of water from the surface during high-recharge time periods. For shallow groundwater, seasonal temperature-driven fluctuations in groundwater TDS may occur (Nelson, 2002).

(b) The Natural pH of Groundwater.

At the typical temperature of groundwater, a pH of 7 is considered neutral. Therefore, a pH less than 7 is acidic and a pH greater than 7 means the water is alkaline. The pH is actually a measure of the hydrogen ion ($H^+$) availability (activity). The hydrogen ion is very small and is able to enter and disrupt mineral structures so that they contribute dissolved constituents to groundwater. Consequently, the greater the $H^+$ availability, i.e., the lower the pH, the higher the TDS in the water. Natural rainwater is slightly acidic because it combines with carbon dioxide ($CO_2$) in the atmosphere, forming carbonic acid ($H_2CO_3$) according to reaction (1) (Krauskopf, 1994):

$$H_2O + CO_2 = H_2CO_3 \qquad (1)$$

Some of the carbonic acid in the rainwater dissociates according to reaction (2), producing bicarbonate ($HCO_3^-$) and $H^+$.

$$H_2CO_3 = HCO_3^- + H^+ \qquad (2)$$

The hydrogen ion produced by reaction (2) lowers the pH of rainwater. How far it lowers it from the neutral value of 7 depends on how much carbonic acid is in the water, which in turn depends on how much carbon dioxide is in the atmosphere. The more $CO_2$ present, the more acidic is the water. For the amount of $CO_2$ in the Earth's atmosphere (~0.3%), the pH of rainwater is about 5.7 (Nelson, 2002).

(c) Oxidizing-Reducing (Redox) Reactions.

Oxidizing-reducing reactions result in a change of the charge of an ion as it gains or loses an electron. These reactions are almost always facilitated by bacteria that are able to gain energy from the reactions. The solubility of some elements in water depends on whether they are oxidized or reduced. The redox potential can be correlated with the amount of dissolved oxygen. As the oxygen content drops, the environment becomes more reducing (the redox potential drops). The natural environment, therefore, may control in which state the element occurs. For example, iron (Fe) can exist in either as reduced ($Fe^{2+}$) or oxidized ($Fe^{3+}$) iron. Iron is more soluble in the reduced state than it is in the oxidized state, where it often forms an iron oxide mineral ($Fe_2O_3$) or iron hydroxide mineral ($Fe[OH]_3$). Therefore, if the local environment produces the reduced iron form, the water will have higher concentrations of iron (Nelson, 2002).

The most common cause of reducing reactions is organic matter, either in solid form or as dissolved organic carbon (DOC). The oxidation of an organic molecule can result in iron, in a solid iron oxide mineral ($Fe_2O_3$), being dissolved into the water as reduced iron ($Fe^{2+}$). Manganese (Mn) behaves in a similar manner to iron. Typically in groundwater, sulfur exists as sulfate ($SO_4^{2-}$). In this form, it generally has little impact on the potability of groundwater (an exception is at much higher concentrations, i.e., 250 mg/L, sulphate may have a laxative affect on some individuals). If, however, the sulfur is in the form of hydrogen sulfide ($H_2S$), the distinct and unpleasant rotten egg odor occurs even at concentrations below 10 mg/L. Redox reactions can change sulphate to hydrogen sulfide in oxygen-poor environments in the presence of organic matter or DOC. With decreasing redox potential the following reducing reactions will occur: nitrate to nitrogen gas, $Fe^{3+}$ (insoluble) to $Fe^{2+}$ (soluble), sulphate to hydrogen sulfide and, at very low redox potential, methane formation (Drever, 1982).

**Aquifers**

Rock beds at the saturated zone that host flowing groundwater are called aquifers. Aquifer rocks contain the water in voids - pores and fissures. The size and number of voids and the degree of interconnection between those pores and fissures define the qualities of the aquifers. The same properties define infiltration efficiency and capacity of intake of recharge water ( Mazor, 2004).

Some of the rock types are:

- Conglomerates:-these rock deposits are made up of rock pebbles cemented to different degrees. If poorly cemented, conglomerates are extremely efficient water intake systems; they form aquifers with large storage volumes, and water flows relatively fast through them. Often conglomerates are cemented by calcite, iron oxides, or silica.
- Sandstone:- is composed of quartz grains with pores constituting 10–50% of the rock volume. The pores are interconnected, providing high infiltration efficiencies and providing sandstone aquifers with high storage capacities and rapid water through flow.

- Limestone and dolomite:- These carbonate rocks are often well crystallized and can be poor in interconnected pores. They tend to fracture under tectonic stress, and through such fractures groundwater can move. Water either fills up the fissures by precipitation of carbonates or, under high flow conditions, the water dissolves the rock and causes further opening. Dissolution of limestone and dolomite may thus create surface and subsurface conduits that enhance intake of recharge water and form high-conducting aquifers with large water storage capacities (Mazor,2004).
- Igneous rocks:- Granite and other intrusive igneous rocks have intrinsically well-crystallized structures with no empty pores. They tend to fracture and may have a limited degree of infiltration capacity and aquifer conductivity. Weathering in humid climates may result in extensive formation of soil, but little dissolution opening of fractures. Thus, granitic rocks may form very poor to medium quality aquifers.

Cementation reduces the water-carrying capacity of an aquifer, and in extreme cases are so tightly cemented that they act as aquicludes. Rock strata that prevent passage of groundwater are called aquicludes . They are important components of groundwater systems because they seal the aquifers and prevent water from infiltrating to great depths. Aquicludes are essential to the formation of springs and shallow accessible aquifers. Aquiclude rocks have low water conductivity caused by a lack of interconnected voids or conduits ( Mazor,2004).

Common aquiclude-forming rocks are;

- Clay:- Clay minerals have several characteristics that make them good aquicludes: They swell, closing desiccation fractures or tectonic fractures and are plastic which makes them effective sealing agents. The thicker the aquiclude, the higher is its sealing efficiency.

Shales are derivatives of clays, formed in slow diagenetic processes. Shales have little or negligible swelling capacity and have medium plasticity. They form effective aquicludes at thicknesses of at least a few meters to tens of meters.

- Igneous rocks:- Large igneous bodies, such as stocks or thick sills, often act as aquicludes because they lack interconnected fractures or dissolution conduits.

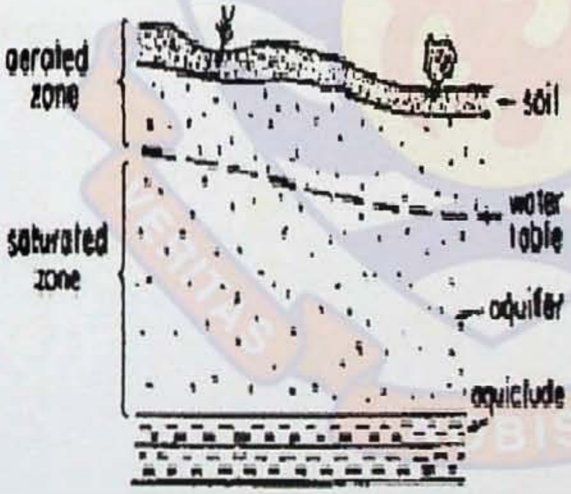


Figure 5: Basic components of a phreatic groundwater system: intake outcrops, an aeratedzone, the water table, the saturated zone that constitutes a water-bearing aquifer, and impermeable rock beds of the aquiclude that seal the aquifer at its base (Mazor, 2004)

### Confined Aquifers and Artesian Flow

Confined aquifers are water-bearing strata that are sealed at the top and the bottom by aquiclude rocks of low permeability (Fig. 6). Confined aquifers are commonly formed in folded terrains and have a phreatic section, where the aquifer rock beds are exposed to recharge infiltration, and a confined section, where the aquifer rock beds are isolated from the landscape surface by an aquiclude. The water in the saturated zone of the phreatic section of a confined system exerts a hydrostatic pressure that causes water to ascend in wells to a level higher than the level at which the water was first struck. In extreme cases the water ascends to the surface, constituting an artesian well ( Mazor, 2004).

Sedimentary basins usually contain a stack of aquifers and aquitards, with an unconfined aquifer at the top and often several confined aquifers below . Typically aquifers are formed by relatively coarse and permeable sand or gravel deposits, whereas very fine clay sediments form nearly impermeable aquitards. However, the distinction between aquifers and aquitards is not absolute, as even aquitards have a non-zero, albeit very low, hydraulic conductivity (Aeschbach-Hertg, 2013).

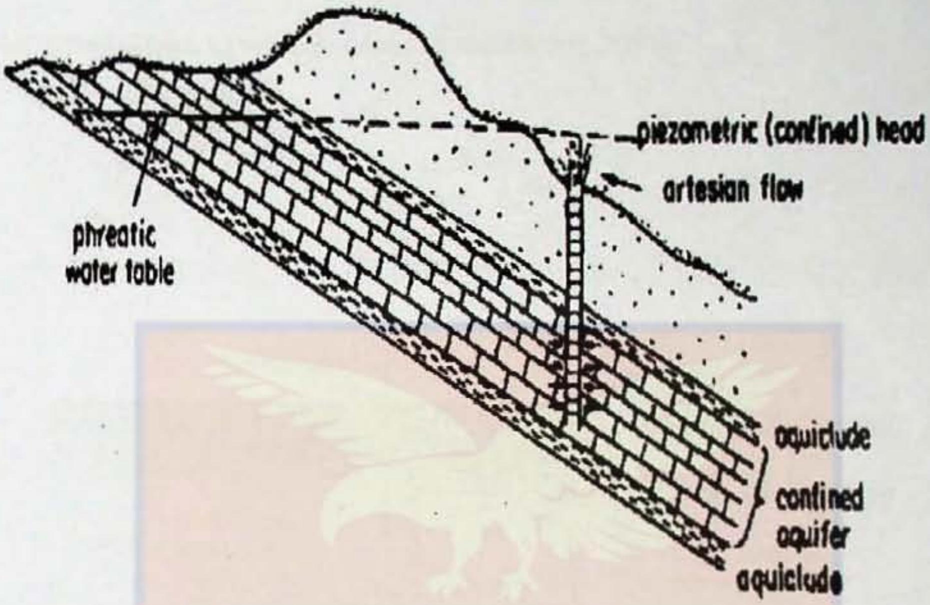


Figure 6: Components of a confined aquifer with through-flow: tilted, or folded, water-bearing rock strata, sealed at the top and the base by aquicludes (Mazor, 2004).

The (potential) height of the water level in an aquifer, i.e., the height to which the water rises in a well, is related to the pressure in the aquifer. It is measured by observing the water level in boreholes, which are called piezometers, hence this height is sometimes called piezometric head, or hydraulic head. The hydraulic head is the height to which the water in an aquifer can rise due to its inner energy (pressure) above its current height $z$.

It can easily be measured by allowing the water to rise in a piezometer. The situation in unconfined and confined aquifers and the terms contributing to *h* are illustrated in Fig. 7. The hydraulic head, i.e. the energy density of the water with respect to weight: (Aeschbach-Hertg, 2013).

$$h = \frac{p}{\rho g} + Z$$

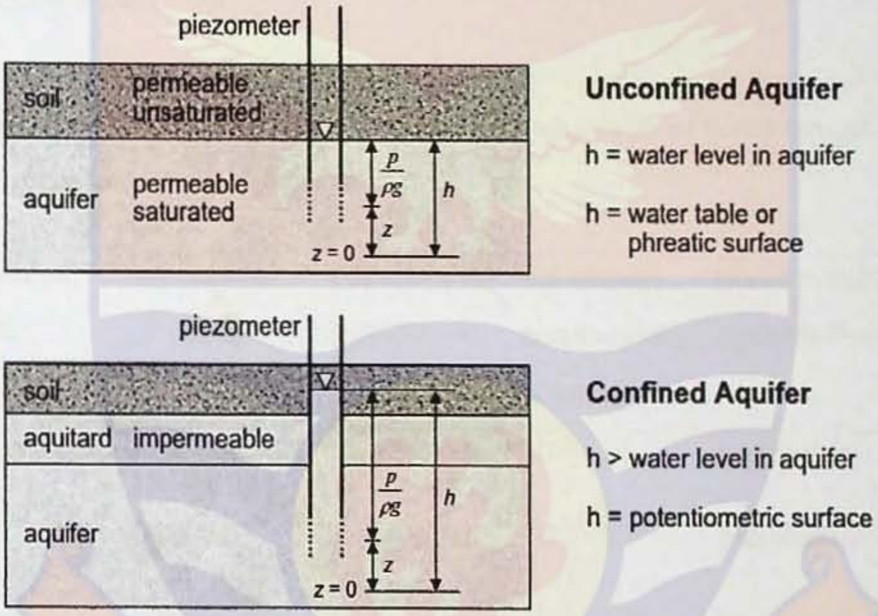


Figure 7: The definition of the hydraulic head in unconfined and confined aquifers (Aeschbach-Hertg, 2013).

### Hydraulic conductivity and permeability

The hydraulic conductivity describes the hydraulic properties of the porous medium, but also depends on the properties of the fluid (viscosity). The permeability *k* has the dimension of an area ($m^2$) and is only a property of the porous medium. It can be parameterised as

$$k = Cd^2,$$

where *d* is the grain size (~ pore size) and C describes a property of the aquifer matrix. This shows that the permeability depends strongly (quadratic) on the grain respectively pore size. On the other hand it does not directly depend on porosity, because porosity is largely independent of grain size. Coarse and fine grained media (e.g. gravel and sand) can have the same porosity but strongly different permeability. Some typical values for grain size, porosity, and hydraulic conductivity of different sediments and rocks are listed in Table 6 (Aeschbach-Hertg, 2013).

Table 6: Grain size, porosity and hydraulic conductivity of some typical aquifer and aquitard materials

| **Sediment, Rock** | **Grain size d [mm]** | **Porosity[%] θ [%]** | **Hydraulic conductivity K [m s]** | **permeability (qualitative)** |
|---|---|---|---|---|
| Gravel (Kies) | >2 | 25-40 | $10^{-2}$ - 10 | permeable |
| Sand | 0.05-2 | 25-50 | $10^{-5}$ - $10^{-2}$ | permeable |
| Silt (Schluff) | 0.002-0.05 | 35-50 | $10^{-9}$ - $10^{-5}$ | halfpermeable |
| Clay (Ton) | <0.002 | 40-70 | $10^{-12}$ - $10^{-9}$ | impermeable |
| Sandstone | - | 5 -30 | $10^{-10}$ - $10^{-5}$ | half-permeable |
| Crystalline rock | - | 0 - 10 | $10^{-13}$- $10^{-11}$ | impermeable |

Source: Aeschbach-Hertg (2013).

**Weathering Reactions**

The natural weathering pathway derived from the reaction of the carbonic acid on minerals to produce dissolved inorganic carbon (mainly $HCO_3^-$) is largely reported in the literature (Probst *et al.*, 1994, 1997; Mortatti *et al.*, 1997; Ludwig *et al.*, 1999)

The two major $CO_2$ consuming weathering reactions are:

(1) the congruent (i.e., complete) dissolution of the major carbonates (e.g. eqn (7) and

(2) the incongruent degradation of the high temperature aluminosilicate minerals in igneous and metamorphic rocks to residual clays, dissolved cations, and silica e.g .the dissolution of albite to kaolinite as in eqn 5. The equations of the dissolution of some other aluminosilicates are presented in equations 4- 6 and 8 (Huh, 2003).

– albite into kaolinite:

$$2NaAlSi_3O_8 + 2CO_2 + 11H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2HCO_3^- + 2Na^+ + 4H_4SiO_4 \quad (3)$$

(Albite) (kaolinite)

– K-feldspar into montmorillonite:

$$2KAlSi_3O_8 + 2CO_2 + 6H_2O \rightarrow Al_2Si_4O_{10}(OH)_2 + 2HCO_3^- + 2K^+ + 2H_4SiO_4 \quad (4)$$

– Ca-plagioclase (anorthite) into kaolinite:

$$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2HCO_3^- + Ca^{2+} \quad (5)$$

(Anorthine) (kaolinite)

– Olivine weathering:

$Mg_2SiO_4 + 4CO_2 + 4H_2O \rightarrow 2Mg^{2+} + 4HCO_3^- + H_4SiO_4$ (6)

– calcite dissolution:

$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^-$ (7)

– pyroxene

$(Ca; Fe; Mg)(SiO_3) + 2H_2O + 2CO_2 \rightarrow \underset{\text{soluble}}{(Ca; Fe; Mg)(HCO_3)_2} + \underset{\text{soluble}}{SiO(OH)}$ (8)

Thus, from weathering reactions above, water containing $HCO_3^-$ indicates $CO_2$-induced interactions with rocks, and the balancing cations indicate the types of rocks encountered. Calcium comes from interaction with limestone, and calcium and magnesium together come from interaction with dolomite; potassium and, even more often, sodium in bicarbonate water come from silicate rocks rich in potassium or sodium feld-spars (Huh, 2003). The processes above commence with the incongruent dissolution of aluminosilicate minerals by $CO_2$ enriched groundwaters, which convert feldspars and micas to kaolin, with a corresponding increase in $Na^+$, $Ca^{2+}$, $K^+$, $Mg^{2+}$, and $H_2SiO_4$ relative to $H^+$ (Stumm & Morgan, 1970). For example equation (3) and (5).

Following further weathering and the increased availability of silica and cations, the kaolinite can then be converted into montmorillonite as follows:

$3.5Al_2Si_2O_5(OH)_4 + Na^+ + 4H_4SiO_4 \Leftrightarrow NaAl_7Si_{11}O_{30}(OH)_6 + H^+ + 11.5\,H_2O$ (9)

(kaolinite) (Na-montmorillonite)

$1.17Al_2Si_2O_5(OH)_4 + 0.167Ca^{2+} + 1.33H_4SiO_4 <=>$

(Kaolinite) $CaO_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 0.33H^+ +$

$3.83H_2O$ (10)

(Ca-montmorillonite)

Predominance diagrams illustrating the typical progress of mineral stability in the weathering process are shown in Figure 8 (from Stumm & Morgan, 1981).

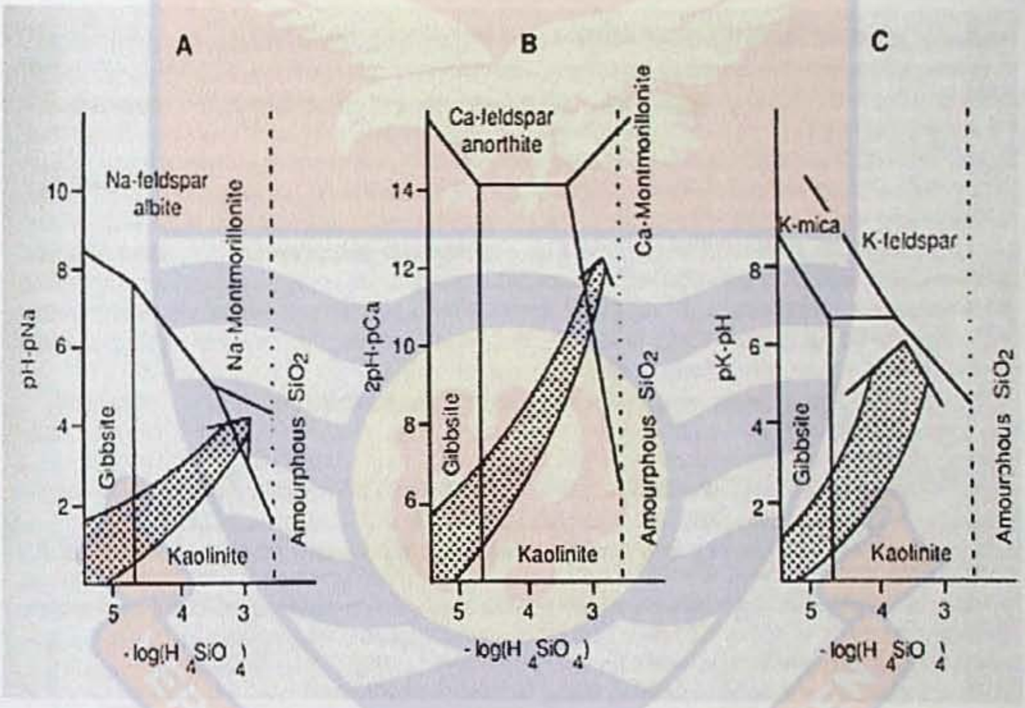


Figure 8: Predominance diagrams illustrating the stability relationships between gibbsite, kaolinite, montmorillonite and feldspars. [Arrows indicate hypothetical paths taken during the weathering process] (after Stumm & Morgan, 1981).

Table 7: Primary source of major ions (Hydrology Project, 1999)

| Ion | Source |
|---|---|
| Calcium | Amphiboles, feldspars, gypsum, aragonite, calcite, pyroxenes, dolomite, clay minerals |
| Magnesium | Amphiboles, olivine, pyroxenes, dolomite, magnesite, clay minerals |
| Sodium | Feldspars, clays, halite, mirabilite, industrial wastes |
| Potassium | Feldspars, feldspathoids, some micas, clays |
| Bicarbonate/ Carbonate | Limestone, dolomite |
| Sulphate | Oxidation of sulphide ores, gypsum, anhydrite |
| Chloride | Sedimentary rock, igneous rock |

## Water Quality Consequences

### Salinity

Salinity is a general term used to describe the presence of elevated levels of different soluble salts such as sodium chloride, magnesium and calcium sulphates and bicarbonates, in soil and water. In some areas, it is a natural component of soil formation and water movement. In other areas, increasing salinity is the result of particular land use practices. Salinity is an important factor in determining many aspects of the chemistry of natural waters and of biological processes within it, and is a thermodynamic state variable that, along with temperature and pressure, governs physical characteristics like the density and heat capacity of the water. Salinity is an ecological factor of considerable importance, influencing the types of organisms that live in a body of water. As well, salinity influences the kinds of plants that will grow either in a water body, or on land fed by a water (or by a groundwater).

Salts are a natural component of our landscape and are derived from four main sources:

i. water evaporated from the sea includes salt which falls with rain over inland areas. Rainfall may deposit these 'cyclic salts' at a rate of up to 6-8 kg/ha/year in coastal regions and is considered to be a major cause of salt accumulation in soil and groundwater of inland areas;

ii. marine sediments derived from inland seas that have retreated over geological time inherently contain large quantities of salts. These 'connate' salts can be subsequently flushed out of the geological material;

iii. the continued weathering of rocks in the process of soil formation often releases salts, particularly in arid regions where there is not enough rainfall to allow flushing through the soil profile. The products of rock weathering can accumulate in the soil profile; and

iv. aeolian deposits, which are sediments deposited by wind, can contain significant stores of salt (Ebbing & Darrell, 1990).

Salinity includes three main forms: dryland salinity, irrigation salinity and saltwater intrusion.

(a) Dryland salinity: This is the buildup of salt in the soil surface in non-irrigated areas. Prior to human settlement, groundwater levels in most were in long-term equilibrium. The clearing of native vegetation has been a key element of rural development in many countries since the early 1800s. The removal of the deep-rooted native vegetation and its replacement, largely by shallow-rooted annual crops and pastures, has resulted in a significant reduction in plant water use. Infiltration of rainfall past the root zone has increased dramatically and large quantities of water are being added to aquifers. This has produced major changes in the water cycle, causing groundwater levels to rise rapidly. Naturally occurring salts become mobilised by being dissolved in the water and brought towards the surface. The large amount of salts moving to the plants' root zone (within 2 m from the surface) affect plant growth, resulting in the dieback of many salt-intolerant species and the encroachment of salt-tolerant species. When the watertable rises to within 1m of the surface, waterlogging and salinisation occurs (NAP, 2001-2008).

(b) Irrigation salinity: occurs on certain irrigated lands resulting from the application of large additional quantities of water, very often without adequate drainage infrastructure to remove excess water. Generally, irrigation areas with inherently low water tables or where lateral drainage is not sufficiently rapid may suffer a rise in groundwater levels resulting in both salinisation and waterlogging. Groundwater within two metres of the soil surface can rise further up the soil profile into the root zone of the crop through capillary action. If groundwater accession continues water will discharge at the soil surface or into surrounding streams, often carrying dissolved salts. Evaporation leaves these salts to accumulate on soil surfaces.

(c) Urban salinity: This results from a combination of dryland salinity processes and over-watering in towns and urban areas. Many rural towns as well as parts of large cities are experiencing the effects of rising watertables, causing salinity and waterlogging. This is resulting in corrosion damage to buildings, amenities and infrastructure such as roads, paths, pipes and bridges.

(d) Seawater intrusion: It is the movement of seawater into fresh water coastal aquifers. It is a natural phenomenon that occurs as a consequence of the density contrast between fresh and saline groundwater. If conditions remain unchanged, the saline water in the aquifer will remain stationary unless it moves under tidal influences. However, when there is excessive pumping of fresh groundwater, sea-level change, or changing recharge conditions, the saline water can gradually move landward within the aquifer until a new equilibrium condition is achieved (Narayan *et al*, 2004). The increasing concentration of human settlements along the coast gives rise to excessive pressure on coastal aquifers (groundwater used for irrigation and consumption, recharge conditions changed due to urban developments), resulting in seawater intrusion and related deterioration of water quality. It is extremely difficult and costly to restore the water quality of an aquifer affected by seawater intrusion. Therefore, it is wiser to plan ahead to prevent seawater intrusion (NAP, 2001-2008).

Management of salinity needs to address the hydrogeological processes controlling salt mobilisation, which requires an integrated understanding of catchment water flows, groundwater dynamics, salt distribution and salt transport processes. Conjunctive water management is the logical approach to salinity mitigation. This can mean incorporating groundwater-surface water connectivity in numerical models used to assess the salinity impacts of new developments or to map management zones around river systems. It can also mean investing in on-ground works such as interception schemes, where bores are operated to pump and remove saline groundwater before it reaches the river (NAP, 2001-2008).

### Hardness

Hardness measures the concentration of multivalent cations, particularly calcium and magnesium, present in a water sample. These ions precipitate easily and may form scale in hot water pipes, water heaters and appliances. They also react with soap to form difficult to remove scum.

Two types of hardness interest water quality analysts: carbonate hardness (temporary) {associated with [$HCO_3^-$] and [$CO_3^{2-}$]} and non-carbonate (permanent) hardness {associated with other anions, particularly [$Cl^-$], [$SO_4^{2-}$]}. When hardness is numerically greater than the sum of bicarbonate and carbonate alkalinity, that amount of hardness equivalent to the total alkalinity (both in units of mg $CaCO_3$ /L) is called the "carbonate hardness"; the amount of hardness in excess of this is the "non-carbonate hardness." When the hardness is numerically equal to or less than the sum of carbonate and non-carbonate alkalinity, all hardness is carbonate hardness and non-carbonate hardness is absent. Water containing calcium carbonate at concentrations below 60 mg/l is generally considered as soft; 60–120 mg/l, moderately hard; 120–180 mg/l, hard; and more than 180 mg/l, very hard (McGowan, 2000).

**Total Dissolved Solids (TDS)**

Total dissolved solids, (TDS) is the term used to describe the inorganic salts and small amounts of organic matter present in solution in water (WHO, 2003). TDS is a measure of the amount of material dissolved in water. This material can include carbonate, bicarbonate, chloride, sulfate, phosphate, nitrate, calcium, magnesium, sodium, organic ions, and other ions.

The presence of dissolved solids in water may affect its taste (Bruvold & Ongerth, 1969). The palatability of drinking water has been rated by panels of tasters in relation to its TDS level as follows: excellent, less than 300 mg/L; good, between 300 and 600 mg/L; fair, between 600 and 900 mg/L; poor, between 900 and 1200 mg/L; and unacceptable, greater than 1200 mg/L

(Bruvold & Ongerth, 1969). Water with extremely low concentrations of TDS may also be unacceptable because of its flat, insipid taste (WHO, 2003).

A certain level of these ions in water is necessary for aquatic life. Changes in TDS concentrations can be harmful because the density of the water determines the flow of water into and out of an organism's cells (Mitchell & Stapp, 1992). However, if TDS concentrations are too high or too low, the growth of many aquatic life can be limited, and death may occur.TDS is used to estimate the quality of drinking water, because it represents the amount of ions in the water. Water with high TDS often has a bad taste and/or high water hardness, and could result in a laxative effect. An elevated TDS indicates the following:

(1) The concentration of the dissolved ions may cause the water to be corrosive, salty or brackish taste, result in scale formation, and interfere and decrease efficiency of hot water heaters; and

(2) Many contain elevated levels of ions that are above the Primary or Secondary Drinking Water Standards, such as: an elevated level of nitrate, arsenic, aluminum, copper, lead, etc.

**Akalinity**

Alkalinity measures the acid-neutralizing capacity (the buffering capacity) of a water sample. The presence of buffering materials help neutralize acids as they are added to the water. These buffering materials are primarily the bases bicarbonate ($HCO_3^-$), and carbonate ($CO_3^{2-}$), and occasionally hydroxide ($OH^-$), borates, silicates, phosphates, ammonium, sulfides, and organic ligands. Alkalinity is used to determine the suitability of water for irrigation, industrial use, raw water characterization and water and wastewater monitoring. Alkalinity in streams is influenced by rocks and soils, salts, certain plant activities, and certain industrial wastewater discharges. Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Living organisms, especially aquatic life, functions best in a pH range of 6.0 to 9.0. For protection of aquatic life, the buffering capacity should be at least 20 mg/L (EPA, 2012).

Alkalinity not only helps regulate the pH of a water body, but also the metal content. Bicarbonate and carbonate ions in water can remove toxic metals (such as lead, arsenic, and cadmium) by precipitating the metals out of solution. Carbonates are added to a water system if the water passes through soil and rock that contain carbonate minerals, such as calcite ($CaCO_3$). Where limestone and sedimentary rocks and carbonate-rich soils are predominant, waters will often have high alkalinity. Where igneous rocks (such as granite) and carbonate-poor soils are predominant waters will have low alkalinity.

### Conductivity

Electrical Conductivity is the ability of a solution to transfer (conduct) electric current. It is the reciprocal of electrical resistivity (ohms). Therefore conductivity is used to measure the concentration of dissolved solids which have been ionized in a polar solution such as water. The unit of measurement commonly used is one millionth of a Siemen per centimeter (micro-Siemens per centimeter or µS/cm). (Heyda, 2008)

Conductivity is a measure of the ability of water to pass an electrical current. Conductivity in water is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulfate, and phosphate anions (ions that carry a negative charge) or sodium, magnesium, calcium, iron, and aluminum cations (ions that carry a positive charge). Organic compounds like oil, phenol, alcohol, and sugar do not conduct electrical current very well and therefore have a low conductivity when in water. Conductivity is also affected by temperature: the warmer the water, the higher the conductivity. For this reason, conductivity is reported as conductivity at 25 degrees Celsius (25 C).

Conductivity in streams and rivers is affected primarily by the geology of the area through which the water flows. Streams that run through areas with granite bedrock tend to have lower conductivity because granite is composed of more inert materials that do not ionize (dissolve into ionic components) when washed into the water. On the other hand, streams that run through areas with clay soils tend to have higher conductivity because of the presence of materials that ionize when washed into the water. Ground water inflows can have the same effects depending on the bedrock they flow through.

**Other Major Ions in Water**

These major ions include Sodium ($Na^+$), high levels of which are often associated with pollution and Potassium ($K^+$) which is generally low (<10 mg/L) in natural fresh waters. Bicarbonate normally ranges from 25 to 400 mg/L and Carbonate in fresh waters is normally dilute (<10 mg/l). The other ions are sulphate, which is normally between 2 and 80 mg/L, Chloride which is normally less than 40 mg/l in unpolluted waters and Nitrate is significant in some areas.

**Sodium**

Sodium is a soft, silvery-white, highly reactive metal that is never found in nature in the uncombined state. Sodium, an alkali-metal element, has a strong tendency to exist in the ionic form. In biological systems and even in solids such as sodium chloride, sodium remains distinctly separate as the sodium ion. sodium is produced primarily as sodium chloride (salt or halite), sodium sulphate (salt cake), and sodium phosphates. The major sources are the underground salt deposits and the naturally occurring brines of lakes (Health Canada, 2012).

Sodium is the most abundant of the alkali elements and constitutes 2.6 percent of the Earth's crust (Weast, 1972). Compounds of sodium are widely distributed in nature. Weathering of salt deposits and contact of water with igneous rock provide natural sources of sodium (OME, 1981). Most soils contain sodium in the range of 0.1 to 1 percent, mainly as silicate minerals such as amphiboles and feldspars. A few soils are "salt affected", containing large amounts of soluble and exchangeable sodium; the solonetzic soils of western Canada contain water-soluble sodium at concentrations up to 9 g/L (Bowser *et al*, 1962). When the sodium content of the soil solution is high, the sodium concentration in the ground water is also usually high and can increase salinity in rivers and streams. Because of the high solubility of sodium minerals, sodium is ubiquitous in the water environment. Sodium concentrations vary considerably depending on regional and local hydrological and geological conditions, the time of year, and salt utilization patterns. In ground waters, sodium concentrations normally range between 6 and 130 mg/L (Bond & Straub, 1973). The use of water-softening chemicals can dramatically increase the sodium concentration. For example, the sodium sulphate concentration of the Edmonton water supply was found to rise from 8 mg/L in summer to 56 mg/L in winter because of the use of lime-soda ash for softening (Elliot & Alexander, 1961).

Production of such industrial chemicals as caustic soda, chlorine, sodium carbonate, sodium chlorate, sodium chlorite, sodium bicarbonate, and sodium hypochlorite accounts for the greatest single use of sodium chloride in Canada (3.5 million tonnes in 1983). Significant quantities are also needed in the food processing, grain milling, slaughtering and meat packing, pulp and paper milling, leather tanning, textile, and brewing industries (Health Canada, 2012).

Industrial consumption of sodium sulphate occurs mainly in the pulp and paper, glass and glass-wool, and soap industries. Sodium sulphate is also employed in lesser amounts in the manufacture of pigments and colours, in base-metal smelting, in the manufacture of medicinal and industrial chemicals, and as a mineral feed supplement (Barry, 1985; Prud'homme, 1985).

Sodium is the most abundant cation in the extracellular fluid. It is largely associated with chloride and bicarbonate in regulation of acid–base equilibrium. Maintenance of the osmotic pressure of body fluid, and thus prevention of excess fluid loss, is another important function of sodium.

Sodium also acts in preserving the normal irritability of muscle and permeability of cells. The minimum sodium chloride requirement is about 120 mg/day (approximately 50 mg of sodium in this form) (WHO, 1984). Water and electrolyte balances are maintained by dietary intake in food and water and loss in urine, faeces, perspiration, expired air, active renal filtration and ion absorption mechanisms (Subramanian, & Méranger, 1984).

Sodium is not considered to be a toxic element. Although numerous studies have shown that reducing sodium intake will lower blood pressure in hypertensives, it cannot be inferred that increased sodium intake will cause hypertension. Generally, the taste of drinking water is offensive at a sodium concentration above 200 mg/L. The aesthetic objective for sodium in drinking water is therefore 200 mg/L (Health Canada, 2012).

### Potassium

Naturally occurring potassium is composed of three isotopes, one of which, $^{40}K$, is radioactive. Traces (0.012%) of this isotope are found in all potassium making it the most common radioactive element in the human body and in many biological materials, as well as in common building substances such as concrete. Elemental potassium does not occur in nature because of its high reactivity. It reacts violently with water and also reacts with oxygen. In its various compounds, potassium makes up about 2.6% of the weight of the Earth's crust and is the seventh most abundant element, similar in abundance to sodium at approximately 1.8% of the crust (Greenwood & Earnshaw, 1997). Potassium in nature occurs only in ionic salts. As such, it is found dissolved in seawater (which is 0.04% potassium by weight), and is part of many minerals. The potassium concentration in seawater is 0.39 g/L (0.039 wt/v%), far less abundant than sodium at 10.8 g/L (1.08 wt/v%) (Anthoni, 2006). Orthoclase ( $KAlSi_3O_8$) is an important tectosilicate mineral which forms igneous rock. Alternate names are alkali feldspar, potassium feldspar and K-feldspar is a common rock-forming mineral. Granite for example contains 5% potassium, which is well above the average in the Earth's crust. Sylvite (KCl), carnallite ($KCl\cdot MgCl_2\cdot 6(H_2O)$), kainite ($MgSO_4\cdot KCl\cdot 3H_2O$) and langbeinite ($MgSO_4\cdot K_2SO_4$) are the minerals found in large evaporite deposits worldwide. The deposits often show layers starting with the least soluble at the bottom and the most soluble on top (Prud'homme & Krukowski, 2006). Deposits of potassium nitrate are formed by decomposition of organic material in contact with atmosphere, mostly in caves; because of the good water solubility of potassium nitrate the formation of larger deposits requires special environmental conditions. Typically, the pure potassium endmember of orthoclase forms a solid solution with albite, the sodium endmember ($NaAlSi_3O_8$), of plagioclase. While slowly cooling within the earth, sodium-rich albite lamellae form by exsolution, enriching the remaining orthoclase with potassium. The resulting intergrowth of the two feldspars is called perthite. Together with the other potassium feldspars orthoclase is a common raw material for the manufacture of some glasses, some ceramics, such as porcelain, and as a constituent of scouring powder. Some intergrowths of orthoclase and albite have an attractive pale luster and are called moonstone when used in jewellery. Most moonstones are translucent and white, although grey and peach-coloured varieties also occur (Schultz *et al.*, 2006).

Most industrial chemical applications of potassium employ the relatively high solubility in water of potassium compounds, such as potassium soaps. Potassium metal has only a few special applications, being replaced in most chemical reactions with sodium metal. For a long time the only significant applications for potash were the production of glass, bleach, soap and gunpowder as potassium nitrate (Shaposhnik, 2007). Potassium soaps from animal fats and vegetable oils were especially prized, as they tended to be more water-soluble and of softer texture, and were known as soft soaps.

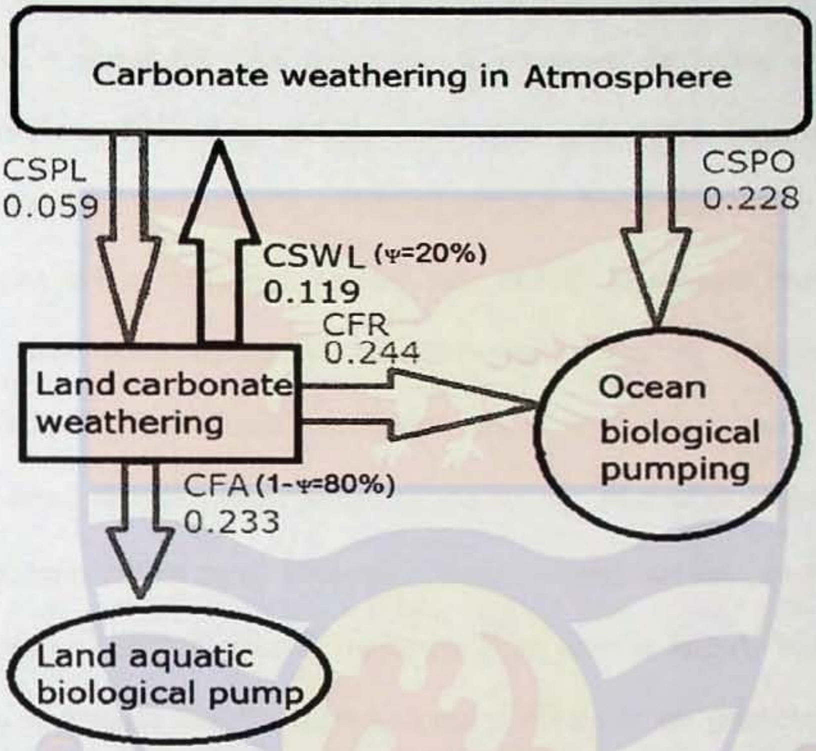
Potassium ions are necessary for the function of all living cells. Potassium ion diffusion is a key mechanism in nerve transmission, and potassium depletion in animals, including humans, results in various cardiac dysfunctions. Potassium accumulates in plant cells, and thus fresh fruits and vegetables are a good dietary source of it. This resulted in potassium first being isolated from potash, the ashes of plants, giving the element its name. For the same reason, heavy crop production rapidly depletes soils of potassium, and agricultural fertilizers consume 95% of global potassium chemical production. Conversely, plants are intolerant of sodium ions and thus sodium is present in only low concentrations, except specialist halophytes (Greenwood & Earnshaw, 1997).

**Calcium:**

Calcium is a soft gray alkaline earth metal, and is the fifth-most-abundant element by mass in the Earth's crust. Calcium is also the fifth-most-abundant dissolved ion in seawater by both molarity and mass, after sodium, chloride, magnesium, and sulfate. Calcium is not naturally found in its elemental state. Calcium occurs most commonly in sedimentary rocks in the minerals calcite, dolomite and gypsum. It also occurs in igneous and metamorphic rocks chiefly in the silicate minerals: plagioclases, amphiboles, pyroxenes and garnets. Calcium provides an important link between tectonics, climate and the carbon cycle. In the simplest terms, uplift of mountains exposes Ca-bearing rocks to chemical weathering and releases $Ca^{2+}$ into surface water. This $Ca^{2+}$ eventually is transported to the ocean where it reacts with dissolved $CO_2$ to form limestone. Some of this limestone settles to the sea floor where it is incorporated into new rocks. Dissolved $CO_2$, along with carbonate and bicarbonate ions, are referred to as dissolved inorganic carbon (DIC). The actual reaction is more complicated and involves the bicarbonate ion ($HCO_3^-$) that forms when $CO_2$ reacts with water at seawater pH:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 \text{ (limestone)} + CO_2 + H_2O$$

At ocean pH, most of the $CO_2$ produced in this reaction is immediately converted back into $HCO_3^-$. The reaction results in a net transport of one molecule of $CO_2$ from the ocean/atmosphere into the lithosphere (Zeebe, (2006). The result is that each $Ca^{2+}$ ion released by chemical weathering ultimately removes one $CO_2$ molecule from the surficial system (atmosphere, ocean, soils and living organisms), storing it in carbonate rocks where it is likely to stay for hundreds of millions of years. The weathering of calcium from rocks thus scrubs $CO_2$ from the ocean and atmosphere, exerting a strong long-term effect on climate. Analogous cycles involving magnesium, and to a much smaller extent strontium and barium, have the same effect. As the weathering of limestone ($CaCO_3$) liberates equimolar amounts of $Ca^{2+}$ and $CO_2$, it has no net effect on the $CO_2$ content of the atmosphere and ocean. The weathering of silicate rocks like granite, on the other hand, is a net $CO_2$ sink because it produces abundant $Ca^{2+}$ but very little $CO_2$ (Berner, 2003) (Fig. 9).



$$\boxed{CaCO_3+CO_2+H_2O=Ca^{2+}+2HCO_3^-=CaCO_3+\Psi(CO_2+H_2O)+(1-\Psi)(CH_2O+O_2)}$$

Figure 9: Atmospheric $CO_2$ sinks (in Pg C/a) by carbonate weathering (i.e., carbonate dissolution, coupled with aquatic photosynthetic uptake of the resulting dissolved inorganic carbon) (Liu *et al.* (2010)).

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CSPL: carbon sink by precipitation on land; CSPO: carbon sink by precipitation in oceans; CSWL: carbon source from waters on land; CFR: carbon flux to oceans by rivers; CFA: carbon flux by aquatic plants to organic matter burial sites

Calcium is essential for living organisms, in particular in cell physiology, where movement of the calcium ion $Ca^{2+}$ into and out of the cytoplasm functions as a signal for many cellular processes. Over 99% of total body calcium is found in bones and teeth, where it functions as a key structural element. The remaining body calcium functions in metabolism, serving as a signal for vital physiological processes, including vascular contraction, blood clotting, muscle contraction and nerve transmission. Calcium plays an important role in building stronger, denser bones early in life and keeping bones strong and healthy later in life. Inadequate intakes of calcium have been associated with increased risks of osteoporosis, nephrolithiasis (kidney stones), colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance and obesity. Most of these disorders have treatments but no cures. Calcium is unique among nutrients, in that the body's reserve is also functional: increasing bone mass is linearly related to reduction in fracture risk. To a great extent, individuals are protected from excess intakes of calcium by a tightly regulated intestinal absorption mechanism through the action of 1,25-dihydroxyvitamin D, the hormonally active form of vitamin D. When absorbed calcium is in excess of need, the excess is excreted by the kidney in most healthy people (WHO, 2009).

Calcium is used:

- as a reducing agent in the extraction of other metals, such as uranium, zirconium, and thorium.
- as a deoxidizer, desulphurizer, or decarbonizer for various ferrous and nonferrous alloys.

- as an alloying agent used in the production of aluminium, beryllium, copper, lead, and magnesium alloys.
- in the making of cements and mortars to be used in construction.
- in the making of cheese, where calcium ions influence the activity of rennin in bringing about the coagulation of milk (Lide, 2005).

**Magnesium**

It is an alkaline earth metal and the eighth-most-abundant element in the Earth's crust and ninth in the known universe as a whole. Magnesium is the fourth-most-common element in the Earth as a whole (behind iron, oxygen and silicon), making up 13% of the planet's mass and a large fraction of the planet's mantle (Housecroft & Sharpe, (2008). Due to magnesium ion's high solubility in water, it is the third-most-abundant element dissolved in seawater. The free element (metal) is not found naturally on Earth, as it is highly reactive (though once produced, it is coated in a thin layer of oxide, which partly masks this reactivity). Magnesium is found in large deposits of magnesite, dolomite, and other minerals, and in mineral waters, where magnesium ion is soluble. Although magnesium is found in over 60 minerals, only dolomite ($CaCO_3 \cdot MgCO_3$), magnesite, brucite, carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), talc, and olivine are of commercial importance (Russell, 2005).

The $Mg^{2+}$ cation is the second-most-abundant cation in seawater (occurring at about 12% of the mass of sodium there), which makes seawater and sea-salt an attractive commercial source of Mg. To extract the magnesium, calcium hydroxide is added to seawater to form magnesium hydroxide precipitate.

$$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaCl_2$$

Magnesium hydroxide (brucite) is insoluble in water, so it can be filtered out and reacted with hydrochloric acid to obtain concentrated magnesium chloride.

$$Mg(OH)_2 + 2\,HCl \rightarrow MgCl_2 + 2\,H_2O$$

The metal is obtained by electrolysis of the magnesium chloride.

The main applications of magnesium are:

- an alloying agent to make aluminium-magnesium alloys, sometimes called magnalium or magnelium. Since magnesium is less dense than aluminium, these alloys are prized for their relative lightness and strength.
- in die-casting (alloyed with zinc) (Baker &Avedesian, 1999),
- to remove sulfur in the production of iron and steel, and the production of titanium in the Kroll process (Ketil *et al*., 2002).

Magnesium is the fourth most abundant cation in the body and the second most abundant cation in intracellular fluid. It is a cofactor for some 350 cellular enzymes, many of which are involved in energy metabolism. The enzymes require the presence of magnesium ions for their catalytic action, including all enzymes utilizing or synthesizing ATP, or those that use other nucleotides to synthesize DNA and RNA. ATP exists in cells normally as a chelate of ATP and a magnesium ion. Because of the important interaction between phosphate and magnesium ions, magnesium ions are essential to the basic nucleic acid chemistry of life, and thus are essential to all cells of all known living organisms. It is also involved in protein and nucleic acid synthesis and is needed for normal vascular tone and insulin sensitivity. Low magnesium levels are associated with endothelial dysfunction, increased vascular reactions, elevated circulating levels of C-reactive Protein and decreased insulin sensitivity. Low Magnesium status has been implicated in hypertension, coronary heart disease, type 2 diabetes mellitus and metabolic syndrome (WHO, 2009). Plants have an additional use for magnesium in that chlorophylls are magnesium-centered porphyrins. Magnesium deficiency in plants causes late-season yellowing between leaf veins, especially in older leaves, and can be corrected by applying Epsom salts or else crushed dolomitic limestone to the soil (Wester, 1987).

## Isotope Hydrology

The term ''isotope hydrology'' signifies the application of techniques that measure isotopic abundances to hydrological problems. The majority of isotope applications in hydrology take advantage of the variations of naturally occurring stable and radioactive isotopes, also referred to as environmental isotopes. The most frequently used environmental isotopes include the heavy isotopes of the elements of the water molecule, hydrogen {$^{2}$H (deuterium), and $^{3}$H (tritium)} and oxygen ($^{18}$O), and of the element carbon ($^{13}$C and $^{14}$C), the latter occurring in inorganic and organic carbon compounds dissolved in water.

Isotopic compositions are expressed conventionally as δ values, representing deviation in per mil (‰) from the isotopic composition of a specified standard, such that

$$\delta^2H \text{ or } \delta^{18}O = 1000 \times [(R\ \text{sample}/R\ \text{standard}) - 1],$$

where R refers to the $^2H/^1H$ or $^{18}O/^{16}O$ ratios in both sample and standard. The most widely used standard in hydrological applications is the Vienna standard mean ocean water (V-SMOW), which approximates the bulk isotopic composition of the present-day global ocean reservoir, and hence has $\delta^2H$ and $\delta^{18}O$ values both defined to be exactly 0‰. Use of the δ scale referenced to V-SMOW also implies that most precipitation and continental waters will have negative values, indicating a lower heavy isotope content compared with the world oceans (Gibson *et al*, 2005).

The stable isotope composition of groundwater reflects that of the precipitation in the recharge area (Gonfiantini *et al*, 1998).This recharge water seeps through the soil and unsaturated zone and eventually reaches the water table. Typically, only a small portion of precipitation may reach the water table, less than about 5 to 25 percent in temperate climates (Clark & Fritz, 1997). Generally, the isotopic composition of water from the saturated zone will closely represent that of the mean annual precipitation (Rank *et al*, 1992; Douglas, 1977).

The $\delta^2H$ and $\delta^{18}O$ of precipitation water are covariant and exhibit distinct seasonal variations. This seasonal signal is due to the strong correlation between temperature and stable isotopes in precipitation and can be used to track the predominant season during which groundwater recharge occurs (Sueker, 2003). Isotope variations in precipitation are generally characterized by strong linear correlations between $^{18}O$ and $^{2}H$ that reflect mass-dependent partitioning of the water isotopes in the hydrological cycle.

Isotopic fractionation of water molecules due to evaporation of seawater and subsequent precipitation in rainfall was recognized by Craig (1961). Based on about 400 water samples from rivers, lakes and precipitation, a linear relationship between deuterium and oxygen-18 was established for average global meteoric waters. This relationship :

($\delta^2H = 8.\delta^{18}O + 10$) is known as the Global Meteoric Water Line (GMWL)

and provides a useful benchmark against which regional or local waters can be compared and their isotopic composition interpreted.

Comparison of the stable isotope data for surface water and groundwater samples relative to the global or local meteoric water lines can provide information on processes. For example, isotopically light water molecules evaporate more efficiently than isotopically heavy water molecules. Due to this variability in isotopic vapour pressures, evaporation produces residual water enriched in the heavier isotopes relative to the initial isotopic composition. Therefore water that has undergone evaporation lies to the right of the local meteoric water line due to this enrichment (Coplen, 1993). Sueker *et al*, (2000) investigated surface and groundwater hydrology at a former gold mine in northeastern Nevada. Most groundwater samples plotted along the MWL indicating that snow-derived water was the primary source of recharge to groundwater. Water in North Fork Humboldt River (NFHR), two pit lakes, and one well downgradient of the lower pit lake had $\delta^2H$ and $\delta^{18}O$ values that systematically diverged from the MWL with a slope of about 5.0, indicating that evaporation was occurring. However, groundwater upgradient from the pit lakes plotted on the MWL. Therefore, it was concluded that some of the water in the well down gradient from the pit lake was derived from the pit lakes and that the pit lakes were actively connected with the local groundwater system (Fig. 10)

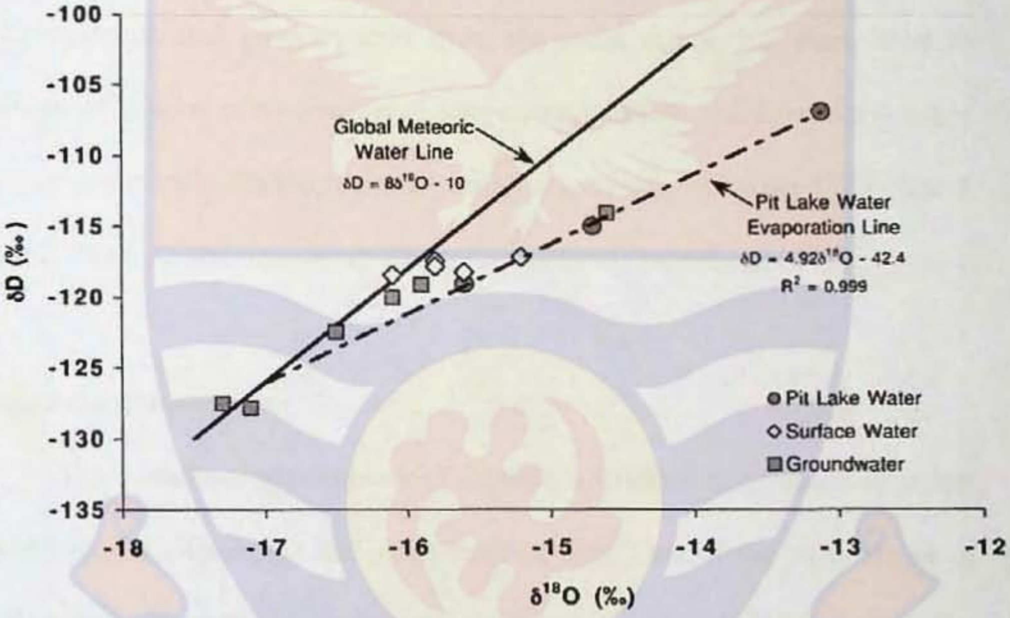

Figure 10: δD and $\delta^{18}O$ of surface-water and groundwater samples collected at the Big Springs Mine, North Fork Humboldt River, Nevada (Sueker *et al*, 2000).

Isotopes of oxygen and hydrogen are in some instances, ideal geochemical traces of underground water because their concentrations are not subject to changes by interaction with the aquifer material. Once the water is underground and removed form zones of evaporation, the isotope ratios do not change, except by mixing. When precipitation infiltrates to recharge the groundwater, mixing in the unsaturated zone controls the isotopic variations.

The water in the saturated zone then has a composition corresponding to the mean isotopic composition of infiltration in the area. Studies of oxygen and hydrogen isotopes in rivers and their tributaries have many applications such as identification of sources(s) of water, assessment of mixing proportions among them and estimation of evaporation loss during their transit ( Ingrahan, 1998). In addition, comparism of stable isotope data of river waters with those of precipitation and groundwaters from the same region has been used to evaluate infiltration of river water to subsurface aquifers and delineate the role of evapotranspiration in the regional precipitation budget (Payne, 1983; Gat & Matsui, 1991; Krishnamurthy & Bhattacharya,1991; Ingraham, 1998).

## Isotopes in groundwater

The numerous applications of isotope hydrological methods applying stable isotopes encompass the entire hydrosphere. One of the main fields of application is concerned with the origin and mixing of groundwater and of its dissolved natural and anthropogenic constituents. Most comprehensive information is obtained from stable isotope abundances. They can be measured quickly and cheaply and can be reliably interpreted as a largely conservative tracer (Gat & Gonfiantini 1981).

### Hydrogeological Structures - Groundwater Regimes

The hydrogeological structure describes the configuration of aquifers and aquicludes within the geological environment. It determines the groundwater circulation from the recharge area, along the percolation and circulation pathways (groundwater reservoir) to the drainage area. The drainage rate in a hydrogeological system depends on the hydraulic gradient or the slope of the piezometric surface. The latter usually changes due to the seasonally variable groundwater recharge (as the fluctuation of groundwater level is controlled by precipitation) or due to anthropogenic influences (e.g. due to pumping of water from the aquifer). Under favourable conditions, a hydrogeological structure contains a usable resource of groundwater.

The economic value depends on the yield (discharge rate of usable groundwater) and the storage volume (water reserve or storage). The complex of conditions which govern the change of the quantitative and qualitative factors of groundwater flow in time and space is called the groundwater regime. Such groundwater regime may be studied by analyses of environmental isotopes, supplementing classical hydrological approaches such as: Radionuclide dating in combination with analyses of stable isotopes may clarify the period and climatic conditions during groundwater recharge (groundwater dating and palaeohydrology; In particular, isotope studies help to determine the origin of the groundwater, to clarify ecological problems related to the hydrological cycle, and to provide information needed for sustainable groundwater management and protection. For the interpretation of isotopic data the actual hydrogeological structure and the groundwater flow system have to be simplified in order to develop a model that may describe the hydrodynamic behaviour. For this task, basic knowledge on the main types of hydrogeological structures is necessary (Mook, 2000).

## Chemicals in groundwater

Chemical compounds are often needed for an unambiguous interpretation of isotope results. The simplest natural chemical tracing of groundwater movement tends to rely on measuring the chloride concentration. $Cl^-$ is a conservative tracer, which is subject, neither to adsorption or desorption during transport. Hence, the relation between chloride concentration and $\delta^{18}O$ or $\delta^{2}H$ values illustrates the effect of various processes such as groundwater mixing (Fig.11), the dissolution of halite or the admixture of saline water, seawater or brine. During hydrochemical evolution the concentration of individual ionic species either increases, remains constant or decreases. For example, in the case of water-rock interaction a $Na^+$ increase along the aquifer flowpath, associated with a decrease in $Ca^{2+}$ and $Mg^{2+}$, is attributed to ion exchange with clay minerals (e.g. Clark & Fritz, 1997); changes in $Ca^{2+}$, $Mg^{2+}$ and $SO_4^{2-}$ are due to anhydrite dissolution and dedolomitisation (e.g. Plummer *et al.* 1994).

The process of incongruent dissolution can have quite different effects on groundwater chemistry depending on the rock type involved (e.g. Gislason and Eugster 1987). In other cases bacterially-mediated redox reactions may occur, commonly resulting in an increase in dissolved $Fe^{2+}$ and $Mn^{2+}$ along the flowpath, and not especially sensitive to the aquifer lithology (e.g. Edmunds *et al.* 1987; Mariotti *et al.* 1988). The identification of the processes is essential for $^{14}C$ groundwater dating. These reactions also modify the $\delta^{13}C$, $\delta^{34}S$ and $\delta^{15}N$ values (Mook, 2000).

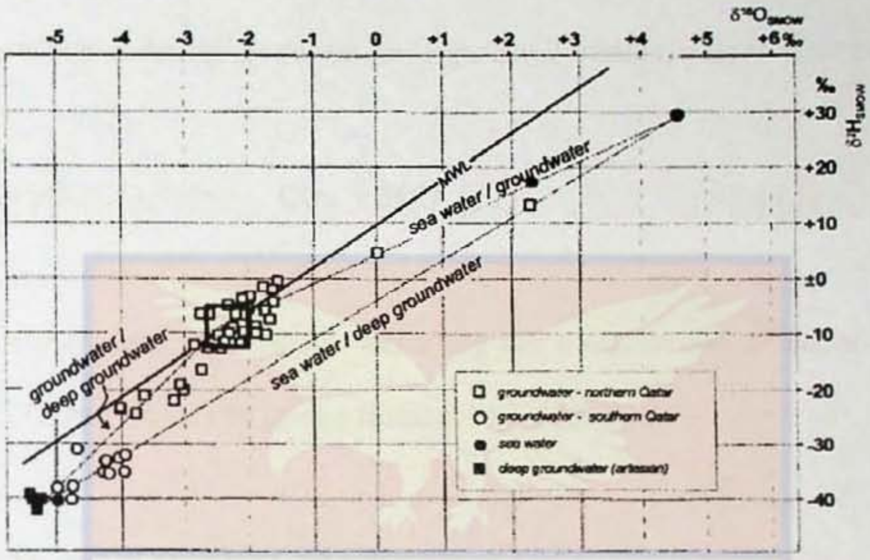

Figure 11: Three-component mixing triangle: three mixing lines of two components each between see water/deep groundwater, sea water/groundwater and deep griouncl/groundwater for Qatar (Yurtsever & Payne, 1979).

**Reactions with organic matter**

The chemical interaction of groundwater and organic matter has an important influence on the carbon isotope composition of the dissolved inorganic carbon compounds in groundwater.

The main processes are:

(1) oxidation of organic matter, with the formation of $CO_2$ and successive chemical reactions with carbonate in the aquifer rock matrix, and

(2) methane genesis.

The oxidation of organic matter (plant remains, coal, peat, lignite) may occur with the dissolved oxygen of freshly recharged groundwater or by sulphate reduction. The $CO_2$ -$HCO_3^-$ system behaves as a closed system, so that the $\delta^{13}C$ and $^{14}C$ values are changed.

Organic carbon in the soil or deeper underground is being oxidised according to:

$$CH_2O + O_2 \iff CO_2 + H_2O \qquad (4.1)$$

This $CO_2$ may dissolve carbonate increasing the concentration of dissolved carbon ($CO_2$ and $HCO_3^-$) by up to a factor of two through:

$$CO_2 + CaCO_3 + H_2O \iff 2HCO_3^- + Ca^{2+} \qquad (4.2)$$

Under organic matter containing soils fresh groundwater typically contains 12 to 24 mg C per litre in the form of dissolved inorganic carbon.

Sulphate reduction may occur according to

$$2CH_2O + SO_4^{2-} \iff 2CO_2 + S^{2-} + 2H_2O \qquad (4.3)$$

100 mg/L $SO_4^{2-}$ may form 91 mg/L $CO_2$ corresponding to a maximum increase of bicarbonate by a factor of 3.

In the first step, oxidation increases Dissolved Inorganic Carbon (DIC) due to the formation of $CO_2$ while $HCO_3^-$ remains constant. The $^{14}C$ and $\delta^{13}C$ values decrease and the $^{14}C$ age increases. In the next step the $CO_2$

concentrations decreases and DIC rises. The $^{14}C$ value decreases while the $^{14}C$ age and the $\delta^{13}C$ value increases. The calculation of the $^{14}C$ age is done by the product of the $^{14}C$ activity and the DIC concentration rather than by the $^{14}C$ activity. That means $^{14}C$ activity per litre of water is used rather than $^{14}C$ activity per gram carbon (Mook, 2000).

The process of methane genesis from organic matter is more complicated. It follows the reaction (Clark and Fritz 1997):

$$2CH_2O <=> CO_2 + CH_4 \qquad (4.4)$$

$CO_2$ and methane are formed of which the latter may develop similar reactions as described before. The concurrent shift in $\delta^{13}C$ is large but rather uncertain, as there is a strong but variable kinetic isotope fractionation involved. Usually the $CO_2$ becomes isotopically enriched in $^{13}C$ which qualitatively allows the identification of this process (Mook, 2000).

Admixture of thermocatalytic, abiogenic or mantle fossil methane is often associated with the admixture of fossil $CO_2$. Gas will expel after exchange with the dissolved $CO_2$, resulting in an uncontrolled loss of $^{14}C$. In any case, methane is rarely found in resources of fresh groundwater (Geyh & Kunzl 1981).

**Water-Rock interactions**

Isotope exchange between groundwater and minerals at temperatures of common, nonthermal groundwater bodies is slow (O'Neil, 1987). Heterogeneous reactions between water and minerals with complex kinetics are usually irreversible at low temperatures. Therefore, cold groundwater rarely reaches chemical and isotopic equilibrium with minerals of the aquifer. There are, however, exceptions. The reaction between water, $CO_2$ and calcite is one example. Others examples are the oxidation of organic material as peat, and microbial metabolic processes which do not only change the chemical composition and oxidation state of dissolved nutrients ($O_2$, C and S), but are also accompanied by large shifts in the isotope compositions (isotope fractionation).

The isotopic and chemical compositions of groundwater reflect the mineralogical composition of the rocks in the aquifer and can be used to localise recharge areas, and to determine the origin of groundwater (meteoric, marine, fossil, magmatic and metamorphic water) and of individual chemical components (e.g. carbonate, sulphate, nitrate and ammonium). The water compositions can also give information about processes of water-rock interaction and microbial processes in the water.

There are three major processes which are accompanied by isotope fractionation of water molecules and dissolved components in groundwater systems within the time scale of groundwater percolation:

(1) evaporation and condensation leading to the fractionation of $^{2}H/^{1}H$ and $^{18}O/^{16}O$ between vapour and liquid water,

(2) chemical reactions between gaseous $CO_2$, dissolved carbonate species and precipitated carbonate minerals leading to the fractionation of $^{13}C/^{12}C$ and $^{14}C/^{12}C$.

(3) microbial metabolic processes such as desulf$ication (Krouse, 1980), denitrification and nitrification (Hubner, 1986), leading to the fractionation of $^{15}N/^{14}N$, $^{34}S/^{32}S$ and $^{18}O$ in anions between solution and organic matter.

In geothermal systems significant isotope exchange of hydrogen and oxygen occurs between rock and water, due to membrane filtration through layers of semi-permeable clays as well as hydration or dehydration of secondary minerals. Because of the slow exchange of isotopes between cold groundwater and its surrounding rock, groundwaters of different origin can preserve their isotopic compositions over geological times. Therefore, mixing of different types of groundwater and the origin of dissolved components can be evaluated using $\delta^2H$, $\delta^{18}O$, $\delta^{34}S$ values and the $^{87}Sr/^{86}Sr$ ratio acting as conservative tracers like chloride and bromide ions. In case of mixing of more than three components it may be difficult to determine the isotopic and hydrochemical compositions of the corresponding end members.

**Hydrochemical Facies:**

Hydrochemical facies describes a group of ground waters with similar composition, and each facies typically has a unique origin and/ or pattern of evolution (Freeze & Cherry, 1979). Ground waters might be assigned to different hydrochemical facies if they are hosted by aquifers of differing lithology or degree of confinement. Hydrochemical facies definitions are typically based on the median values of many different parameters, and thus assignment of a groundwater to single facies is a convenient way to summarize a vast amount of multivariate time-series data on water quality (Daughney & Revees, 2005). In addition to providing a means to simplifying data from a groundwater monitoring programme hydrochemical facies assignments offer other benefits for resource management.

Assignment of a groundwater to a hydrochemical facies provides some insights into the environmental processes that have affected a site in the past, and might continue to do so in the future. In this manner facies assignments also provides a means of distinguishing pristine ground waters from ground waters affected by human activity. The baseline (i.e., normal or background) range of concentration for each analyte in each facies can be determined separately, simplifying identification of sites with anomalous concentrations that might indicate human impact (Daughney & Revees, 2005).

### Piper Diagrams

The Hydrochemical evolution of groundwater can be understood by plotting the major cations and anions in the Piper trilinear diagram (Piper, 1944). This diagram reveals similarities and differences among groundwater samples because those with similar qualities will tend to plot together as groups (Todd & Mays, 2005). This diagram is very useful in bringing out chemical relationships among groundwater in more definite terms.

In the Piper Diagram cations, expressed as percentages of total cations in milliequivalents per liter, plots as a single point on the left triangle and anions, similarly expressed as percentages of total anions, appear as a single point in the right triangle. These two points are then projected into the central diamond-shaped are parallel to the upper edges of the central area. This single point is thus uniquely related to the total ionic distribution (Fig. 12).

Hydrochemical facies are distinct zones that have cation and anion concentrations describable within defined composition categories. The definition of a composition category is commonly based on subdivisions of the trilinear diagram in the manner suggested by Back (1961) and Back and Hanshaw (1965). These subdivisions are shown in Figures 12 and 13.

The geochemical evolution can be understood from the Piper plot, which has been divided into six sub categories viz. 1 (Ca-$HCO_3$ type); 2 (Ca-Cl type); 3 (Na-Cl type); 4 (Na-$HCO_3$ type); 5 (Mixed Ca-Na-$HCO_3$ type) and 6 (Mixed Ca-Mg-Cl type) as shown in fig. 13.

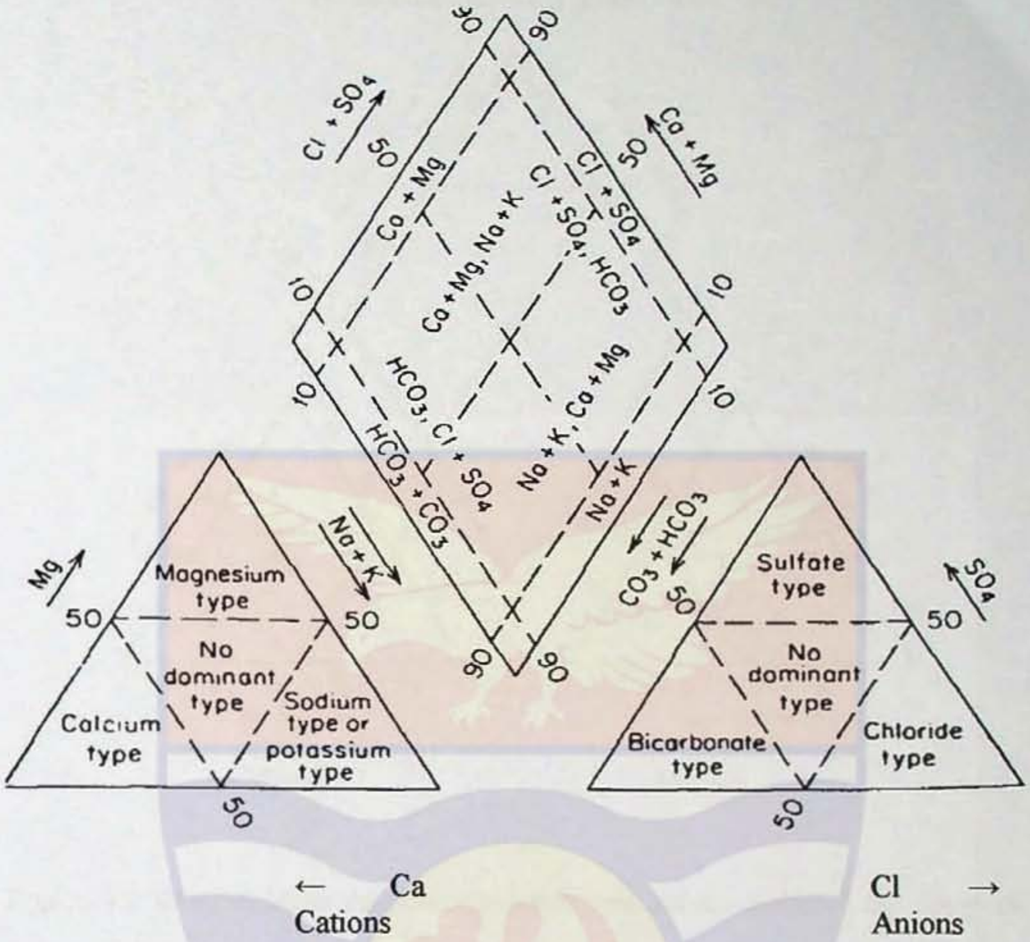

Figure 12: Classification diagram for anion and cation facies in terms of major- ion percentages (Freeze & Cherry, 1979).

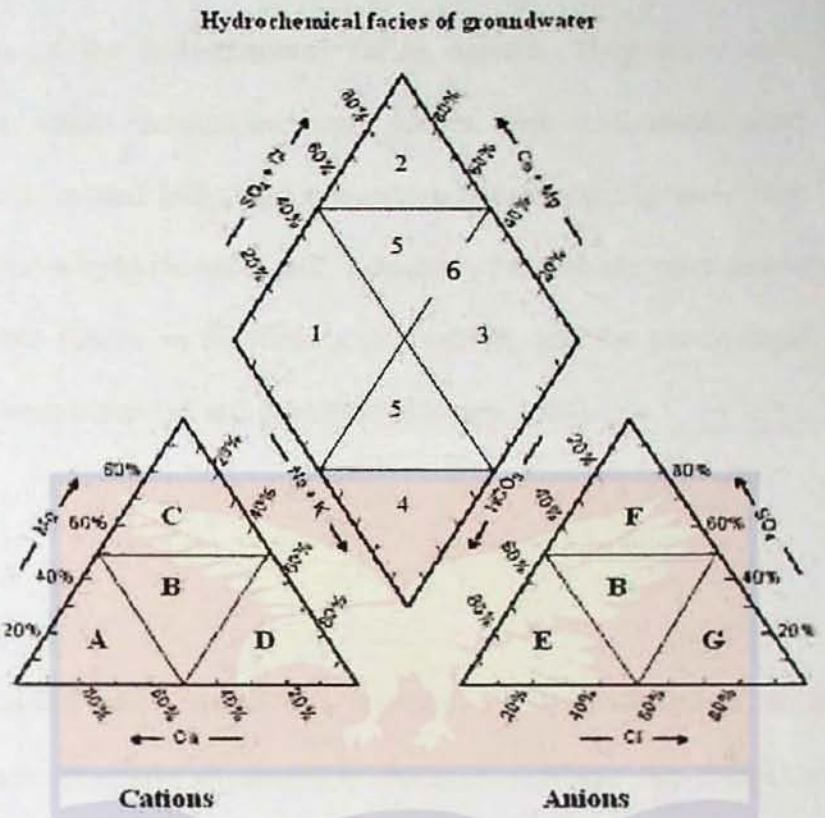

Figure 13: Classification diagram for anion and cation facies in the form of major-ion percentages (Sadashivaiah *et al.*, 2008).

**Legend**

A- Calcium type

B- No Dominant type

C- Magnesium type

D- Sodium and potassium type

E- Bicarbonate type

F- Sulphate type

G- Chloride type

1- Magnesium- bicarbonate

2- Calcium- chloride type

3- Sodium- Chloride type

4- Sodium- bicarbonate type

5- Mixed Ca-Na-$HCO_3$ type

6- Mixed Ca-Mg-Cl type

Mixed- type (No cation- anion exceed 50%)

Trilinear diagrams were used in this study as the first step in the classification of the hydrochemical facies present. They were used to determine in which stratigraphic units waters were sufficiently close in composition to assume hydrologic connection between stratigraphic units to permit study as a hydrochemical unit. Therefore, the analyses were converted from parts per million to equivalents per million, and the per-centages of equivalents were computed and were plotted (Back, 1961).

## Trace Metals

Numerous trace metals are essential dietary components at low concentrations for aquatic organisms; however, trace metals also pose a threat to organisms due to their persistence in sediments, toxicity at high concentrations, and tendency to bioaccumulate in aquatic ecosystems (Censi *et al*., 2006). Lead, chromium, cadmium, copper, zinc, and mercury are trace metals that are commonly enriched in sediments due to anthropogenic activities (Kennish 1992). Trace metals have been referred to as common pollutants, which are widely distributed in the environment with sources mainly from weathering of minerals and soils (Merian, 1991).

Anthropogenic activities like mining, ultimate disposal of treated and untreated waste effluents containing toxic metals as well as metal chelates (Amman, *et al.*, 2002) from different industries, e.g. tannery, steel plants, battery industries, thermal power plants etc. and also the indiscriminate use of heavy metal containing fertilizers and pesticides in agriculture resulted in deterioration of water quality rendering serious environmental problems posing threat on human beings (Lantzy & Mackenzie, 1979) and sustaining aquatic biodiversity (Ghosh & Vass, 1997). Though some of the metals like Cu, Fe, Mn, Ni and Zn are essential as micronutrients for life processes in plants and microorganisms, while many other metals like Cd, Cr and Pb have no known physiological activity, but they are proved detrimental beyond a certain limit (Bruins, *et al.*, 2000).

### Zinc

Zinc is chalcophile and occurs almost exclusively in compounds together with other elements. In igneous and sedimentary rocks it occurs in the structure of silicates and oxides. The most abundant Zn minerals are sphalerite (ZnS), smithsonite ($ZnCO_3$), and also zincite (ZnO). Zinc is strongly adsorbed to colloidal matter in streams and rivers, explaining the very high Zn contents in these solids. In aqueous solutions, zinc forms moderately strong complexes with oxygen-containing ligands. The free $Zn^{2+}$ ion dominates at pH <7.5 and $ZnCO_3$ at higher pH leading to limited solubility both under oxic and anoxic conditions. Solid ZnS forms under anoxic conditions in the presence of sulphur, and ZnO/ $ZnCO_3$ solids form under toxic conditions and high pH (>7.5).

Although (Zn) has been found to have low toxicity to man, prolonged consumption of large doses can result in some health complications such as fatigue, dizziness and neutropenia (Hess & Schmid, 2002). Some literature sources have also reveal that Zn could be toxic to some aquatic organisms such as fish (Alabaster & Lloyd, 1980). The free zinc ion in solution is highly toxic to plants, invertebrates, and even vertebrate fish (Eisler, 1993). The Free Ion Activity Model is well-established in literatures, and shows that just micromolar amounts of the free ion kills some organisms. A recent example showed 6 micromolar killing 93% of all *Daphnia* in water (Muyssen *et al.*, 2006).

Zinc is an essential trace element, necessary for plants (Broadley *et al.*, 2007), animals (Prasad, 2008) and microorganisms (Sugarman, 1987). Zinc is found in nearly 100 specific enzymes (other sources say 300), and serves as structural ions in transcription factors and is stored and transferred in metallothioneins. It is the only metal which appears in all enzyme classes (Broadley *et al.*, 2007). Zinc is distributed throughout the human body (Rink & Gabriel, 2000). Most zinc is in the brain, muscle, bones, kidney, and liver, with the highest concentrations in the prostate and parts of the eye (Wapnir & Raul, 1990). Semen is particularly rich in zinc, which is a key factor in prostate gland function and reproductive organ growth (Berdanier *et al.*, 2007). Although zinc is an essential requirement for good health, excess zinc can be harmful. Excessive absorption of zinc suppresses copper and iron absorption (Fosmire, 1990). Certain metals such as Cu and Co are classified as essential to life due to their involvement in certain physiological processes. Elevated levels of these, however, have been found to be toxic (Spear, 1981).

**Cadmium**

Cadmium (Cd) is a highly toxic trace element, which enters the environment mainly from industrial processes and phosphate fertilisers.

Cadmium (Cd) has many similarities to zinc, but it is far less abundant. Cadmium is also chalcophile, and is almost always associated with Zn in ore deposits and other earth material. Cadmium metal is used mainly as an anticorrosive, electroplated onto steel. Cadmium sulphide and selenide are commonly used as pigments in plastics. Cadmium compounds are used in electric batteries, electronic components and nuclear reactors (Friberg *et al.*, 1986; Ros & Slooff, 1987).

Sources of Cd include wastes from Cd-based batteries, incinerators and run-off from agricultural soils where phosphate fertilizers are used since Cd is a common impurity in phosphate fertilizers (Stoeppler, 1991). Higher levels are present in sedimentary rocks: marine phosphates often contain about 15 mg/kg. Weathering and erosion result in the transport by rivers of large quantities of cadmium to the world's oceans and this represents a major flux of the global cadmium cycle; an annual gross input of 1000 tones has been estimated (ATSDR, 2007). Cadmium concentration can reach high levels in agricultural soils and is easily assimilated by plants. When taken up in excess by plants, Cadmium induces various visible symptoms of phytotoxicity, e.g., leaf roll, chlorosis and necrosis, growth retardation, browning of root tips, and finally death (Kahle, 1993; Namdjoyan *et al.*, 2012; Tran & Popova, 2013).

Cadmium is one of the most toxic with reported carcinogenic effects in humans (Goering *et al*, 1994). It accumulates mainly in the kidney and liver and high concentrations have been found to lead to chronic kidney dysfunction. It induces cell injury and death by interfering with Calcium (Ca) regulation in biological systems. It has been found to toxic to fish and other aquatic organisms (Woodworth & Pascoe,1982). Cadium has been implicated in endocrine disrupting activities, which could pose serious health problems. Apart from the health implications, the metal (Cd), together with other metals, e.g. Zn form a toxic "soup" that often acts synergistically. Cd ions are known to affect the structure and function of chloroplasts in many plant species such as *Triticumaestivum* (Atal *et al.*, 1991), *Beta vulgaris* (Greger & Ögren, 1991), *Vigna radiate* (Keshena & Mukherji, 1992), *Spinaceaoleracea* (Sersen & Kral'ova, 2001), and *Phaseolus vulgaris* (Padmaja *et al.*, 1990).

A large number of studies have demonstrated that the primary sites of action of Cd are photosynthetic pigments, especially the biosynthesis of chlorophyll (Baszynski *et al*, 1980) and carotenoids (Prasad, 1995). According to Baryla *et al*, (2001), the observed chlorosis in oilseed rape was not due to a direct interaction of Cd with the chlorophyll biosynthesis pathway and most probably it was caused by decreasing of chloroplast density.

The solubility of cadmium in water is influenced to a large degree by its acidity; suspended or sediment-bound cadmium may dissolve when there is an increase in acidity (Ros & Slooff, 1987). In natural waters, cadmium is found mainly in bottom sediments and suspended particles (Friberg *et al.*, 1986).

**Aluminium**

Aluminium (Al) is the most abundant metal in the Earth's crust (8.4% by weight), and the third most abundant element after oxygen and silicon. It is lithophile, and a major constituent of many rock-forming minerals, such as feldspars and micas, where it substitutes for Si in tetrahedral coordination with oxygen. Clay minerals, as one of the weathering products of primary rocks, contain the highest amounts of aluminium, up to 25% by weight. Weathering of alumino-silicates results in the formation of a range of secondary minerals, such as Al-goethite and gibbsite (van Helvoort *et al*, 2007).At low pH, Al occurs as free $Al^{3+}$, and at pH > 6, it forms the very insoluble $Al(OH)_3$ solid (gibbsite). Several Al-OH complexes add up to the total aqueous speciation of Al; in order of dominance with increasing pH: $AlHO^{2+}$, $Al(OH)_2^{+}$, $Al(OH)_4^{-}$. Aluminium does not take part in redox reactions at all. Concentrations in groundwater are strongly pH dependent (Nordstrom, 1982) and it is most unlikely that high aluminium will be found in well-buffered carbonate-containing lithologies. Hitchon *et al.* (1999) report a background concentration in the ppb range.

Aluminium metal is used as a structural material in the construction, automotive, and aircraftindustries, in the production of metal alloys, in the electric industry, in cooking utensils, and in food packaging. Aluminium compounds are used as antacids, antiperspirants, and food additives (ATSDR, 1992). Aluminium salts are also widely used in water treatment as coagulants to reduce organic matter, colour, turbidity, and microorganism levels. The process usually consists of addition of an aluminium salt (often sulfate) at optimum pH and dosage, followed by flocculation, sedimentation, and filtration (Health Canada, 1993).

Table 8: Aluminium contents in rocks and sediments and phosphate minerals,

| Material | Al content (formula) |
|---|---|
| crust | 8.4 % |
| Igneous rocks | |
| granite (Ca rich – Ca poor) | 7.2 - 8.2 % |
| basalt | 8.3 % |
| Sediments | |
| shale | 8.0 % |
| sandstones | 2.5 % |
| limestones | 0.4 % |
| Aluminium minerals (other than rockforming minerals and clay minerals) | |
| Alunite | $KAl_3(SO_4)(OH)_6$ |
| Al-Goethite | $AlOOH$ |
| Gibbsite | $Al(OH)_3$ |
| Kaolinite | $Al_2Si_2O_5(OH)_4$ |

Source: Hitchon *et al.* (1999).

An area in which myriad studies have been conducted regarding aluminum as an environmental factor is the correlation between the number of diagnosed Alzheimers Disease (AD) cases and the aluminum levels in public drinking water. In a study conducted by McLachlan and colleagues (1996), it was found that a relationship did exist between the number of diagnosed AD cases and the level of aluminum present in the drinking water supply. This study concluded that between 15,180 and 26,910 of the estimated 66,000 to 117,000 cases of AD might have been prevented if the aluminum concentration in the municipal water supply had been kept below 100 micrograms per liter. A similar study performed by Jacqmin and associates (1994) using different variables showed no significant effect for aluminum in drinking water when pH was not included in the experiment model, but showed a small relationship between aluminum and AD when pH was also taken into consideration.

Aluminum chloride may corrode the skin, irritate the mucous membranes in the eyes, and cause perspiration, shortness of breath and coughing. Alum increases blood clotting. Dissolved $Al^{3+}$-ions are toxic to plants; these affect roots and decrease phosphate intake. Aluminum is not a dietary requirement for plants, but it may positively influence growth in some species. It is taken up by all plants because of its wide distribution in soils. Aluminum naturally occurs in waters in very low concentrations but higher concentrations derived from mining waste may negatively affect aquatic biocoenosis. Aluminum is toxic to fish in acidic, unbuffered waters starting at a concentration of 0.1 mg/L. Simultaneous electrolyte shortages influence gull permeability, and damage surface gull cells. Aluminum is mainly toxic to fish at pH values 5.0-5.5 and aluminum ions accumulate on the gulls and clog these with a slimy layer, which limits breathing. An aluminum concentration of 1.5 mg/L turned out to be fatal to trout. The element also influences growth of freshwater bony fish (Emsley, 2003; Mason, 2002).

Table 9: Sources and mobilization processes of aluminium

| Source/ process | Natural environment | Anthropogenic / polluted environment |
|---|---|---|
| weathering of Al -silicates | no specific environment | |
| dissolution of Al-oxides, kaolinite, clay minerals | possibly acidic thermal waters (pH,4) | acidified aquifers, especially unconfined, non-calcareous aquifers only to shallow depth |
| | | aquifers affected by acid mine drainage or leachates from colliery wastes |

Source: van Helvoort *et al* (2006-2007).

Table 10: Sinks and immobilisation processes of aluminium

| Sink/ process | Natural waters | Antropogenic/ polluted |
|---|---|---|
| precipitation of secondary Al-silicates, Al-oxides, or Al-sulphates | virtually all groundwaters with pH >4virtually all | virtually all groundwaters with pH>4 |
| adsorption to DOC | DOC rich waters | DOC rich waters |

Source: van Helvoort *et al* (2006-2007).

**Copper**

Copper has an average abundance in the crust of 25 ppm, and its oxidation state is mainly +2 although Cu$^+$ complexes do occur in nature. In the sedimentary cycle, Cu is associated with clay minerals and organic rich sediments such as shales and deep sea clays. Copper is also enriched in the late, hydrothermal stages of magmatic crystallization forming chalcocite ($CuS_2$) and covellite ($CuS$). Copper forms strong complexes with oxygen ligands and with sulphur depending on acidity and redox conditions. Complexes with natural organic substances are also very strong with O and N as ligand atoms. At pH <6, free Cu$^{2+}$ is dominant but complexes with Cl$^-$ and SO$_4^{2-}$ will be significant at high Cl$^-$ and SO$_4^{2-}$ concentrations. Under reducing conditions where sulphide species may occur, CuS and CuS$_2$ will limit conditions where sulphide species may occur, CuS and $CuS_2$ will limit solubility (van Helvoort, 2006). Copper is an essential element in plants and animals (including humans), which means it is necessary for us to live. Therefore, plants and animals must absorb some copper from eating, drinking, and breathing. Copper is an essential nutrient that is incorporated into a number of metalloenzymes involved in hemoglobin formation, drug/xenobiotic metabolism, carbohydrate metabolism, catecholamine biosynthesis, the cross-linking of collagen, elastin, and hair keratin, and the antioxidant defense mechanism. Copper-dependent enzymes, such as cytochrome-c oxidase, superoxide dismutase, ferroxidases, monoamine oxidase, and dopamine β-monooxygenase, function to reduce activated oxygen species or molecular oxygen (ATSDR, 2004). Copper compounds are also used as food additives (e.g. nutrient and/or colouring agent) (US FDA, 1994). Copper sulfate pentahydrate is sometimes added to surface water for the control of algae (NSF, 2000).

Although copper homeostasis plays an important role in the prevention of copper toxicity, exposure to excessive levels of copper can result in a number of adverse health effects including liver and kidney damage, anemia, immunotoxicity, and developmental toxicity. Many of these effects are consistent with oxidative damage to membranes or macromolecules. Copper can bind to the sulfhydryl groups of several enzymes, such as glucose-6-phosphatase and glutathione reductase, thus interfering with their protection of cells from free radical damage (ATSDR, 2004). One of the most commonly reported adverse health effect of copper is gastrointestinal distress. Nausea, vomiting, and/or abdominal pain have been reported, usually occurring shortly after drinking a copper sulfate solution, beverages that were stored in a copper or untinned brass container, or first draw water (ATSDR, 2004). In workers involved in grinding and sieving copper dust, anorexia, nausea, and occasional diarrhea were reported (Suciu *et al*., 1981); exposure levels ranged from 111 to 434 mg Cu/m$^3$ over a 3-year period. It is likely that the observed gastrointestinal effects were due to oral exposure to copper. There are numerous reports of acute gastrointestinal effects in humans after ingestion of large amounts of copper in drinking water or beverages. The most prevalent effects are nausea and vomiting, which typically occur shortly after ingestion and are not persistent (Pizarro *et al*., 1999). Abdominal pain and diarrhea have also been reported, but their incidence is typically much lower than nausea and vomiting (Araya *et al.* 2001).

Several human studies have examined the possible relationship between increased serum copper levels and an increased risk of coronary heart disease. Although a number of studies have found increased risk of coronary heart disease deaths with increasing serum copper levels (Ford, 2000), a number of studies have not found a relationship. There are limited data on the toxicity of copper to the cardiovascular system. A significant increase in systolic blood pressure was observed in rats exposed to 14 mg Cu/kg/day as copper carbonate in the diet for 15 weeks (Liu & Mederios, 1986). No histological alterations were observed in the hearts of rats or mice exposed to 285 or 717 mg Cu/kg/day, respectively, for 14 days or 134 or 814 mg Cu/kg/day for 90 days (NTP, 1993).

### Manganese

Manganese (Mn) is an element widely distributed in the earth's crust. Manganese does not occur naturally in a pure state; oxides, carbonates and silicates are the most important manganese-containing minerals. The most common manganese mineral is pyrolusite ($MnO_2$), usually mined in sedimentary deposits by open-cast techniques. Manganese occurs in most iron ores. It has been determined that manganese is needed for the functioning of key enzymes that play a role in cellular protection from damaging free radical species, maintenance of healthy skin, and synthesis of cholesterol (Friedman *et al.*, 1987). Based upon case-studies in people with low blood manganese and known requirements in animals, it is thought that manganese may also play a role in bone mineralization, metabolism of proteins, lipids, and carbohydrates, energy production, metabolic regulation, and nervous system functioning (Wedler, 1994).

Manganese is also important in photosynthetic oxygen evolution in chloroplasts in plants. The oxygen evolving complex (OEC) is a part of Photosystem II contained in the thylakoid membranes of chloroplasts; it is responsible for the terminal photooxidation of water during the light reactions of photosynthesis and has a metalloenzyme core containing four atoms of manganese. For this reason, most broad-spectrum plant fertilizers contain manganese (Dismukes *et al.*, 2006). A recent study has determined that Mn increases the activity of 3-hydroxy-3-methylglutaryl coenzyme A, the rate limiting enzyme for cholesterol biosynthesis, and that bilirubin decreases cholesterol 7-hydroxylase, which is important in the conversion of cholesterol into bile acids. Modulation of these enzymes results in increased total cholesterol and decreased bile acid production. Acute liver toxicity was noted in steers after Mn infusion into the duodenum for up to 30 h. The bovine liver's capacity to remove Mn by first pass elimination was only exceeded when mesenteric vein infusions occurred at 84 mmol/min. (In a steer of approximately 200 kg, this rate is about 0.42 mmol/kg/min.) (Janelle & Wei, 2004).

It has been determined that manganese is needed for the functioning of key enzymes that play a role in cellular protection from damaging free radical species, maintenance of healthy skin, and synthesis of cholesterol (Friedman *et al.*, 1987).

### Iron (Fe)

The most common iron ore is hematite ($Fe_2O_3$), from which iron metal is obtained by reduction with carbon. Iron is also found in minerals such as taconite and magnetite, which is commonly seen as black sands along beaches and stream banks. It is the second most abundant metal in the earth's crust, of which it accounts for about 5%. Elemental iron is rarely found in nature, as the iron ions $Fe^{2+}$ and $Fe^{3+}$ readily combine with oxygen- and sulfur-containing compounds to form oxides, hydroxides, carbonates, and sulfides. Iron is most commonly found in nature in the form of its oxides (Elinder *et al.*, 1986).

Iron is a key mineral for human metabolism. The healthy human body contains between 2.5 g (40 mg/kg: menstruating woman) and 4.0 g (50 mg/kg: adult male) iron. About 60% is found in the haemoglobin of the red blood cells, and 15% in myoglobin (in muscles) and various enzymes. Haemoglobin and myoglobin are proteins specialised in the transport and storage of oxygen (Baynes, 1994). Iron is a component of several metaloproteins and plays a crucial role in vital biochemical activities, such as oxygen sensing and transport, electron transfer, and catalysis. The biological functions of iron are based on its chemical properties, e.g., its capacity to form a variety of coordination complexes with organic ligands in a dynamic and flexible mode, and its favorable redox potential to switch between the ferrous, Fe(II), and ferric, Fe(III), states. In cellular respiration, it functions as essential component of enzymes involved in biological oxidation such as cytochromes and is an important constituent of succinate dehydrogenase as well as a part of the haeme of haemoglobin (Hb), myoglobin and the cytochromes (Soetan *et al.*, 2010).

Iron is required for proper myelination of spinal cord and white matter of cerebellar folds in brain and is a cofactor for a number of enzymes involved in neurotransmitter synthesis. Iron is involved in synthesis and packaging of neurotransmitters, their uptake and degradation into other iron-containing proteins which may directly or indirectly alter brain function (Soetan *et al.*, 2010). Iron is toxic to cells in excessive amounts. Acute iron poisoning is common and potentially lethal in dogs, cats, and many other animals. Iron is also a leading cause of unintentional poisoning deaths in children less than 6 years old (Jay, 2006).

The efficiency of Fe(II) as an electron donor and of Fe(III) as an electron acceptor, with a redox potential compatible with the constrains of the cellular environment, is a fundamental feature for many biochemical reactions and renders iron to an essential mineral and nutrient. However, this very property turns iron into a potential biohazard, because under aerobic conditions, iron can readily catalyze the generation of noxious radicals (Pantopoulos & Papanikolaou, 2004). Free radicals are highly reactive species and may promote oxidation of proteins, peroxidation of membrane lipids, and modification of nucleic acids. Likewise, reactive nitrogen species, such as peroxynitrite, may lead to protein damage via nitration. Iron typically damages cells in the heart, liver and elsewhere, which can cause significant adverse effects, including coma, metabolic acidosis, shock, liver failure, coagulopathy, adult respiratory distress syndrome, long-term organ damage, and even death (Tenenbein, 1996).

### Chromium

Chromium does not occur freely in nature. The main chromium mineral is chromite. In dissolved form chromium is present as either anionic trivalent $Cr(OH)_3$ or as hexavalent $CrO_4^{2-}$. The amount of dissolved $Cr^{3+}$ ions is relatively low, because these form stable complexes. In natural waters trivalent chromium is most abundant. Many chromium compounds are relatively water insoluble. Chromium (III) compounds are water insoluble because these are largely bound to floating particles in water. Chromium (III) oxide and chromium (III) hydroxide are the only water soluble compounds. Chromium (VI) oxide is an example of an excellently water soluble chromium compound.

Chromium and its salts are used in the leather tanning industry, the manufacture of catalysts, pigments and paints, fungicides, the ceramic and glass industry, and in photography, and for chrome alloy and chromium metal production, chrome plating, and corrosion control (EPA,1987; IARC, 1980; WHO, 1988). The element and its compounds can be discharged in surface water through various industries as it is applied for example for metal surface refinery and in alloys. Stainless steel consists of 12-15% chromium. The metal industry mainly discharged trivalent chromium whilst hexavalent chromium in industrial wastewaters mainly originates from tanning and painting. Chromium compounds are applied as pigments, and 90% of the leather is tanned by means of chromium compounds.. Chromium may be applied as a catalyser, in wood impregnation, in audio and video production and in lasers. Chromite is the starting product for inflammable material and chemical production and chromium may be present in domestic waste from various synthetic materials (Enghag, 2004; Greenwood & Earnshaw, 2002).

Chromium is a dietary requirement for a number of organisms. This however only applies to trivalent chromium. Hexavalent chromium is very toxic to flora and fauna. Chromium (VI) compounds are toxic at low concentrations for both plants and animals. Trivalent chromium is an essential trace element for humans. Together with insulin it removes glucose from blood, and it also plays a vital role in fat metabolism. Chromium deficits may enhance diabetes symptoms. Chromium can also be found in RNA. Chromium deficits are very rare, and chromium feed supplements are not often applied. Chromium (III) toxicity is unlikely, at least when it is taken up through food and drinking water. It may even improve health, and cure neuropathy and encephalopathy. It causes allergic and asthmatic reactions, is carcinogenic and is 1000 times as toxic as trivalent chromium. Health effects related to hexavalent chromium exposure include diarrhoea, stomach and intestinal bleedings, cramps, and liver and kidney damage. Hexavalent chromium is mutagenic. Toxic effects may be passed on to children through the placenta (Ramade, 1987; Raiswell, 1980).

### Other major ions and Nutrients

#### Chloride

Chloride is lithophile and the most abundant halogen in the continental crust. In nature, it accumulates in terminal water reservoirs (oceans, and closed-basin lakes), because it behaves as a conservative substance. As a result, three quarters of crustal chloride occurs in the oceans. In igneous rocks, it probably replaces OH- in apatites, micas, and hornblendes. Evaporites are the main source of chloride where it forms soluble salts such as halite (NaCl) and potassium chloride (KCl); 60% and 40% respectively (Hitchon *et al.*, 1999). Chloride occurs predominantly as the free Cl- ion, and due to its strong electronegativity, it is not affected by pH and redox conditions. Chloride is an inert constituent and concentrations are derived either from rainfall with a degree of evaporative concentration during recharge.

High chloride concentrations in groundwater (see Table 12 below) are due to additions from internal sources – either marine formation waters, recent seawater of dissolution of marine evaporates; locally thermal waters may be significant. Elevated chloride concentrations (e.g. ~200-250 mg/L; Banaszuk

Table 11: Chloride contents in rocks and unconsolidated materials

| Material | Cl content |
|---|---|
| crust | 130 ppm |
| Igneous rocks | |
| granite (Ca rich – Ca poor) | 130-200 ppm |
| basalt | 55 ppm |
| Sediments | |
| shale | 180 ppm |
| sandstones | 10 ppm |
| limestones | 150 ppm |
| Evaprorites (salts) | |
| KCl | 46 % |
| NaCl | 60 % |

Source: Hitchon *et al.* (1999).

There are many anthropogenic sources of chloride in groundwater, but in most cases chloride ion concentrations do not exceed 1000 mg/L (Hitchon, 1999). Application of fertilizers or manure is thought to be an important diffuse source of chloride beneath arable land. Sodium chloride is widely used

There are many anthropogenic sources of chloride in groundwater, but in most cases chloride ion concentrations do not exceed 1000 mg/L (Hitchon, 1999). Application of fertilizers or manure is thought to be an important diffuse source of chloride beneath arable land. Sodium chloride is widely used in the production of industrial chemicals such as caustic soda, chlorine, sodium chlorite, and sodium hypochlorite. Sodium chloride, calcium chloride, and magnesium chloride are extensively used in snow and ice control. Potassium chloride is used in the production of fertilizers (DNHW, 1978).

The toxicity of chloride salts depends on the cation present; that of chloride itself is unknown. Although excessive intake of drinking-water containing sodium chloride at concentrations above 2.5 g/litre has been reported to produce hypertension (Fadeeva, 1971), this effect is believed to be related to the sodium ion concentration. Chloride toxicity has not been observed in humans except in the special case of impaired sodium chloride metabolism, e.g. in congestive heart failure (Wesson, 1969). Healthy individuals can tolerate the intake of large quantities of chloride provided that there is a concomitant intake of fresh water. Little is known about the effect of prolonged intake of large amounts of chloride in the diet. As in experimental animals, hypertension associated with sodium chloride intake appears to be related to the sodium rather than the chloride ion (DNHW, 1978).

Chloride increases the electrical conductivity of water and thus increases its corrosivity. In metal pipes, chloride reacts with metal ions to form soluble salts (WHO, 1978), thus increasing levels of metals in drinking-water. In lead pipes, a protective oxide layer is built up, but chloride enhances

Table 12: Chloride concentrations in water

| Water type | chloride (mg/l) |
|---|---|
| rain water | 3.8 |
| stream water | 7.8 |
| groundwater | 1 – 250 |
| groundwater (polluted) | up to 15000 |
| groundwater (maximum) | up to 180000 |
| formation water (maximum) | up to 403000 |
| thermal water | up to 30000 |

Source: Hitchon (1999).

Some examples of brines, thermal circulation, and water-rock interactions (or combinations) are given below (van Helvoort *et al*, 2006-2007):

- Conti *et al*., (2000) give an overview on the geochemistry of formation waters in the Po plain (northern Italy). The presence of brackish groundwaters results from mixing of meteoric water with deep-seated brines and subsequent upwelling to the surface due to a weak geothermal circulation system. Extreme chloride concentrations in the deep groundwaters influenced by brines reach up to 118600 mg/l, whereas shallow groundwaters with a larger share of meteoric water may have up to ~8000 mg/l.

- Bein & Arad (1992) discuss saline groundwaters occurring in the Baltic region through freezing of seawater during glacial periods. The brines typically occur in crystalline and

- Bein & Arad (1992) discuss saline groundwaters occurring in the Baltic region through freezing of seawater during glacial periods. The brines typically occur in crystalline and metamorphic rocks below fresh groundwater in various localities in Sweden and Finland. High total dissolved solids (up to 20 g/l in Sweden, and 120 g/l in Finland) are indicators of high chloride concentrations up to 16800 mg/l. The brines are subsequently gradually diluted by fresh postglacially infiltrated groundwater. Another example of very high salinity groundwaters was reported by Grobe & Machel (2002). In the Münsterland Cretaceous Basin (Germany) where chlorine concentrations up to 62000 mg/l resulted from evaporite (halite) dissolution.

- In Granitic rocks there is the possibility that some Cl addition results from water-rock interaction with rock-forming minerals rich in volatiles. Such cases are infrequent, but described for example from the Carnmenellis Granite (Cornwall, UK) by Edmunds e*t al.*, (1984). Cl concentrations up to 11500 mg/l are found in thermal waters (around 54°C) and the saline groundwaters are encountered in tin mines, and attributed to hydrolysis of Cl-rich biotites in the thermal aureole.

- Hot Thermal waters as a source of high Cl Concentrations have been discussed by many workers in several countries. A Good example comes from Valentino & Stanzione (2003), who describe some important Cl sources for groundwater associated with thermal activity:
  - (i) Inflow of magmatic HCl Gas into deeply circulation groundwaters;
  - (ii) intensified rock leaching due to high temperatures;
  - (iii) Uptake of seawater or marine components in powerful deep circulation systems.

The Combined effects of these processes led to very high Cl Concentrations (up to 18150 mg/l) in thermal groundwaters beneath the Phlegraean Fields (Naples, italy) (an Helvoort *et al*, 2006-2007).

Table 13: Sources and mobilisation processes of chloride

| Source/ Process | Natural environment | Anthropogenetic/ Polluted environment |
|---|---|---|
| dissolution of evaporites | evaporites | - |
| degassing of magma | deep thermal waters | - |
| seawater intrusion | sea level changes coastal aquifers | overexploited coastal aquifers |
| thermal circulation | thermal waters | - |
| leaching, rainwater infiltration, atmospheric deposition | uinconfined aquifers | unconfined aquifers in urban and agricultural regions |
| evapotranspiration | - | - |

Source: van Helvoort *et al* (2006-2007).

There are no sinks for chlorine in groundwater

### Nitrogen (Nitrate and Ammonium)

#### General geochemistry

Over 73% of the Earth's nitrogen occurs as either $N_2$ or $N_2O$ in the atmosphere (Table 10.0). The oxidation state of nitrogen ranges from -3 to +5. The most abundant valency states in nature are 0 (74.8% as $N_2$), -3 (25.2% as $NH_3$) and +5 (trace, as $NO_3^-$). Nitrogen is a trace constituent of rocks and minerals and Table 14.0 lists the contents of $NH_3$ and $NO_3^-$ in rocks and sediments. According to Wlotzka (1961), all igneous rocks have about the same $NH_3$ content (20ppm), but there are differences for sedimentary rocks. Because nitrogen in sedimentary rocks is primarily associated with organic matter, highest contents are found in clays and shales. Nitrate is present in negligible quantities in most rock types but small amounts are found in saline clays and limestone. Nitrogen minerals are rarely found in nature because they are readily soluble; however, they are formed in sediments formed in highly oxidising environments as evaporite minerals (van Helvoort *et al*, 2006-2007).

#### Aqueous chemistry

Nitrogen can occur in three inorganic ionic forms in groundwater:

- Nitrate ($NO_3^-$) is the dominant form of nitrogen in oxidized groundwater. This is also the predominant form used by plants. Microorganisms convert nitrate to ammonium.
- Ammonium ($NH_4^+$) is the dominant form of nitrogen in anaerobic groundwater. This ammonium is either taken up by plants or oxidized to nitrite and to nitrate, during nitrification.

- Nitrite ($NO_2^-$) is an intermediate form of nitrogen that usually occur at very low concentrations in groundwater (Appelo & Postma, 1996).

Organic nitrogen can also occur in groundwater.

Table 14: Nitrogen content, species and valency in the Earth

| Medium | N species | N abundance (%) | $NH_3$ / $NO_3^-$ (ppm) |
|---|---|---|---|
| Atmosphere | $N_2$, $N_2O$ | 73.1 | - |
| Igneous rocks | $NH_3$, $N_2$ | 12.3 | 20 / 0 |
| Sediments | $NH_3$, N(org.) | 14.2 | - |
| clays & clay slates | - | - | 580 / 5-20 |
| sandstones | - | - | 135 / 0 |
| limestones | - | - | 70 / 5-20 |
| Biosphere | N(org.) | <0.001 | - |
| Hydrosphere | $N_2$, $NO_3^-$, $NH_3$ | 0.4 | - |
| Coal | $NH_3$ | 0.01 | - |
| Nitrate deposits | $NO_3^-$ | 0.00001 | - |

Source: Hitchon et al. (1999) and Wlotzka (1961).

In rivers unaffected by anthropogenic inputs, nitrate concentrations are typically <0.4 mg/L. Background values for nitrate in groundwater are difficult to establish, since many aerobic aquifers possibly containing background nitrate have been contaminated by anthropogenic nitrate sources. Rodvang & Simpkins (2001) reported extreme nitrate concentrations (100-400 mg/L) in groundwaters from organic-rich sedimentary rocks (Canada and several locations in USA). The occurrence of high nitrate groundwaters is associated with organic-rich shales, which bear $NH_3$ derived from mineralized organic nitrogen. There is also widely reported high nitrate from semi-arid regions where nitrogen accumulates in the unsaturated zone, percolating slowly to groundwater, associated with fixation by leguminous vegetation (Edmunds & Gaye 1997).

Several anthropogenic nitrogen sources are possible. The most important and wide-spread nitrogen sources are the application of inorganic fertilisers and manure from intensive live stock breeding on arable land and grass land. Nitrate is leached into the groundwater system via runoff or infiltration, especially in phreatic sandy aquifers and also in major carbonate aquifers such as the Chalk. Non-agricultural nitrogen sources may also lead to extreme nitrate and ammonium concentrations. Other $N_2$ contamination sources include atmospheric deposition of NOx, and mobilisation of $N_2$ from the soil in large excavations at building sites promoting oxidation of organic $N_2$ (see Tables 15 and 16).

Nitrate is used mainly in inorganic fertilizers. It is also used as an oxidizing agent and in the production of explosives, and purified potassium nitrate is used for glass making. Nitrate is sometimes also added to food to serve as a reservoir for nitrite. Nitrates occur naturally in plants, for which it is a key nutrient. Nitrate is also formed endogenously in mammals, including humans. Nitrate is secreted in saliva and then converted to nitrite by oral microflora. Nitrogen in the form of nitrate is taken up by plants and used as nitrogen source in synthesizing amino acids and proteins (WHO, 2011). Surplus nitrate readily moves with the groundwater (USEPA, 1987; van Duijvenboden & Matthijsen, 1989).

The toxicity of nitrate to humans is mainly attributable to its reduction to nitrite. The major biological effect of nitrite in humans is its involvement in the oxidation of normal Hb to metHb, which is unable to transport oxygen to the tissues. The reduced oxygen transport becomes clinically manifest when metHb concentrations reach 10% of normal Hb concentrations and above; the condition, called methaemoglobinaemia, causes cyanosis and, at higher concentrations, asphyxia. The normal metHb level in humans is less than 2%; in infants under 3 months of age, it is less than 3% (WHO, 2011). The Hb of young infants is more susceptible to metHb formation than that of older children and adults. A dose of nitrite causes a higher metHb formation in these infants than in adults. With respect to exposure to nitrate, these young infants are also more at risk because of a relatively high intake of nitrate in relation to body weight and, under certain conditions, a higher reduction of nitrate to nitrite by gastric bacteria as a result of the low production of gastric acid (FAO/WHO, 1996). Other groups potentially susceptible to metHb formation include pregnant women and people deficient in glucose-6-phosphate dehydrogenase or metHb reductase (Speijers *et al*., 1989).

Table 15: Sources and mobilisation processes of ammonium and nitrate in the subsoil

| Source/ process | Subsurface conditions | Natural environment | Anthropogenic / polluted environment |
|---|---|---|---|
| $NH_4^+$ release by organic matter decay | | in top soil | - |
| $NH_4^+$ release by cation exchange or desorption from clays or micas | reduced and near neutral pH | any natural aquifer containing clay mineral exchangers | any aquifer containing clay mineral exchangers |
| nitrification of $NH_4^+$ | oxic, unsaturated zone | in natural soils | intense in fertilized soils |
| nitrification of $NH_4^+$ | sub(oxic), fringe of contaminated groundwater plume | | below/downstream landfills, septic tanks gasworks |
| leaching of $NO_3^-$ | oxic to suboxic | below natural soils, into phreatic aquifers | below fertilised soils into phreatic aquifers |
| $NH_3$ release by High temperature dissolution of igneous rocks | reduced, high temperature | geothermal areas | |

Source: van Helvoort *et al* (2006-2007).

Table 16: Sinks and immobilisation processes of ammonium and nitrate in the subsoil

| Sink/ process | Subsurface conditions | Natural environment | Anthropogenic / polluted environment |
|---|---|---|---|
| adsorption of $NH_4^+$ | reduced, pH 5-8 | any natural aquifer containing clay minerals exchangers | below/ downstream landfills,septic tanks, gasworks |
| $NO_3^-$ conversion to $N_2$ by denitrification | reduced, low $O_2$ (< 0.2 mg/l) | clayey or sandy aquifers/ aquitards with shallow groundwater table, labile organic matter and/ or inorganic reduced species; riparian buffer zones; river bank infiltrate | |
| $NO_3^-$ conversion to $NH_4^+$ by assimilatory reduction | Reduced | reduced aquifers with $NO_3^-$ – poor groundwaters | |

Source: van Helvoort *et al* (2006-2007).

### The mobility of nitrogen in groundwater

The fate of nitrogen species in groundwater, is related to how nitrogen is cycled through the natural environment – the atmosphere, biosphere, soil systems, and hydrosphere. The basic cycle is shown in Figure 14. Nitrogen is an essential nutrient for plant and animal growth and it is taken up by plants from the atmosphere. With the decay of dead organic matter, $NH_4^+$ is released to the soil, where the nitrification process transfers ammonium into nitrite and nitrate. Since these oxidised nitrogen species – nitrate in particular – are highly mobile, they may subsequently leach to the groundwater, if in excess for the vegetation. Nitrate under persistent aerobic conditions remains inert and may remain in solution for hundreds or thousands of years (Edmunds, 1999). In deep groundwaters, the reduction of nitrate to $N_2$ gas (denitrification) takes place, being released eventually to the soil atmosphere, closing the cycle. Thus, nitrification and denitrification are the principal processes governing the N - speciation and mobility in aquifers (van Helvoort *et al*, 2006-2007.

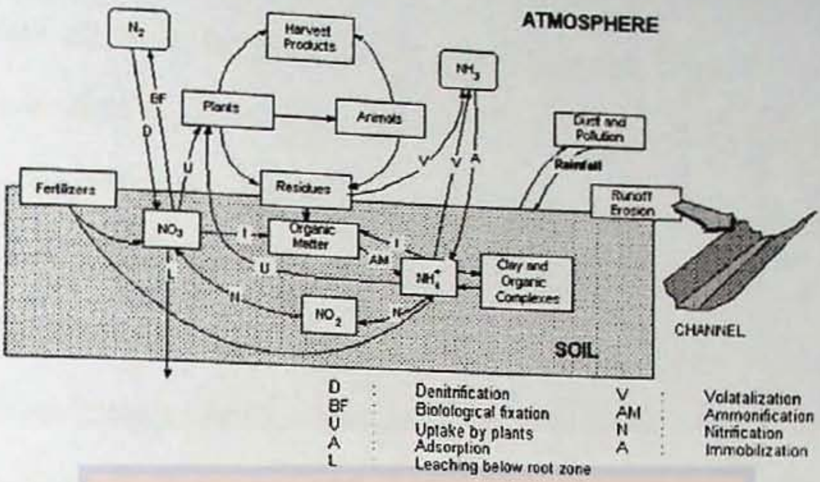

Figure 14: The nitrogen cycle and N-transformations between and within the soil, water and atmosphere compartments (Frere & Leonard, 1982).

The processes of nitrification and denitrification depend on a range of environmental factors. Feast *et al.* (1998) indicate that the optimal conditions for denitrification require availability of reductants, $O_2$ below 0.2 mg/l and pH in the range 7-8. Denitrification is bacterially mediated and therefore nutrients should be present as well (Hiscock *et al.*, 1991). Denitrification proceeds by heterotrophic and autotrophic bacteria, which oxidise organic material (eg. Dissolved Organic Ccarbon, DOC, & Soil Organic Carbon, SOC) or inorganic material (eg. $Fe^{2+}$, sulphur, pyrite), respectively. Examples of heterotrophic (reaction a) and autotrophic (reaction b) denitrification are given below:

$$5CH_2O + 4NO_3^- + 4H^+ \leftrightarrow 2N_2 + 5CO_2 + 7H_2O \qquad (a)$$

$$5FeS_2 + 14NO_3^- + 4H^+ \leftrightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O \qquad (b)$$

High denitrification rates and efficient nitrate removal from groundwater are typically found in topographically low areas with slow moving and shallow groundwater tables favouring anaerobic conditions. Typically, denitrification occurs in a narrow zone at or near the redox boundary (redoxcline), where the amount of electron donors in pore water and sediment increase over a short distance (e.g. Pedersen *et al.*,1991). Reducing conditions are found especially in young sedimentary aquifers rich in organic carbon. Rodvang & Simpkins (2001) conclude that unweathered Quaternary aquitards have the highest denitrification potentials with high amounts of labile organic matter and pyrite, protecting underlying aquifers for a long time from nitrate contamination. Denitrification is also intense in riparian zones, which have high ecological activity or during (natural or artificial) bank filtration due to active slurry within the river bed (Hiscock & Grischek, 2002). In sandy Quaternary aquifers denitrification is observed under anaerobic conditions, but capacity for denitrification may be much lower as reductants may be sparse and readily exhausted. In general, nitrate reduction seems to be most effective in sediments with high contents of labile organic matter or inorganic reductants (van Helvoort *et al*, 2006-2007).

### Sulphur (sulphate and sulphide)

In nature, sulphur occurs in four oxidation states (-2, 0, +4, and +6), two of which (-2, +6) are common in geological materials. Sulphur is the primary constituent of two major mineral groups: sulphides and sulphates. In igneous rocks, sulphur occurs mostly as metallic sulphides, and is rather evenly distributed in the various rock types. In arid sedimentary basins, the highest abundance is in evaporites (gypsum, anhydrite). Coal is also an important bearer of sulphur, both as pyrite and organic matter (e.g. peat). In shales, sulphur occurs mainly as pyrite or similar iron sulphides. In reduced unconsolidated sediments, both freshwater and marine, sulphur is also commonly found as sulphides. Depending on pH and redox conditions, sulphur mainly occurs as sulphate ($SO_4^{2-}$, $HSO_4^-$), or sulphide species ($H_2S$, $HS^-$) in aqueous solutions. In most surface and shallow groundwaters with only mildly reducing conditions, sulphate is the dominant species, since protonated sulphate $HSO_4^-$ is only stable at extremely low pH. Under stronger reducing conditions, sulphate is reduced to $H_2S$ ($pH < 7$) or HS- ($pH > 7$) (van Helvoort *et al*, 2006).

Sulphates occur naturally in numerous minerals, including barite ($BaSO_4$), epsomite ($MgSO_4 \cdot 7H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) (Greenwood and Earnshaw, 2002). These dissolved minerals contribute to the mineral content of many drinking waters. Sulphate solubility could be limited by the formation of many different solids containing (alkali) metals including Al, Ba, Ca, Cu, Fe, Pb, Mg, Mn, Hg, K, Ag, Na, Sr, and Zn, and most of these are fairly soluble in water. Some exceptions are $BaSO_4$, and $SrSO_4$, and the minerals gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$), the latter two being very abundant in nature. Some of the key sulphur transformations are given below:

Pyrite oxidaton:

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 8SO_4^{2-} + 4Fe^{2+} + 16H^+ + 4Fe(OH)_3$$

Sulphate reduction by organic matter:

$$2CH_2O + SO_4^{2-} + H+ \rightarrow HS^- + 2CO_2 + 2H_2O$$

Sulphide precipitation:

$$Fe^{2+} + HS^- \rightarrow FeS + H^+$$

Table 17: The most common sulphur minerals

| | Group | Formula |
|---|---|---|
| sulphides ($^{2-}$) | | |
| | Pyrite | FeS |
| | Arsenopyrite | FeAsS |
| | Chalcopyrite | FeCuS |
| | Cinnabar | HgS |
| | Galena | PbS |
| | Sphalerite | ZnS |
| sulphates ($S^{+6}$) | | |
| | Anhydrite | $CaSO_4$ |
| | Gypsum | $CaSO_4 \cdot 2HO$ |
| | Barite | $BaSO_4$ |
| | Jarosite | $KFe_3(SO_4)_2(OH)_6$ |

Source: van Helvoort *et al* (2006-2007)

The main anthropogenic sources of sulphate in groundwater are associated with mining of sulphide minerals, application of agrochemicals, and contemporary acid rain or fall out input. High sulphate concentrations could also be caused by the oxidation of sulphide-bearing aquifer material where anthropogenic intervention in the natural hydrological regime leads to aeration of the subsurface. Sulphide oxidation, seawater intrusion is another process that increases sulphate concentrations as found in many over-pumped coastal aquifers. 1362 mg/L sulphate was found in shallow phreatic aquifers (Santos *et al.*, 2002). Minor sulphate contamination could be found under arable lands, where the main source is excess fertilisers infiltrating in the aquifer.

Table 18: Sulphate concentrations in natural waters

| Water type | sulphate (mg/l) |
|---|---|
| rain water | ~0.60 |
| stream water | 11 |
| groundwater | 1 – 250 |
| groundwater (polluted) | 33000 |
| groundwater (maximum) | >55000 |
| formation water | 9200 |
| thermal water | ~3200 |

Source: Hitchon (1999).

Sulphates and sulphuric acid products are used in the production of fertilizers, chemicals, dyes, glass, paper, soaps, textiles, fungicides, insecticides, astringents and emetics. They are also used in the mining, wood pulp, metal and plating industries, in sewage treatment and in leather processing (Greenwood & Earnshaw, 2002). Aluminium sulphate (alum) is used as a sedimentation agent in the treatment of drinking-water. Copper sulphate has been used for the control of algae in raw and public water supplies.

There have been a number of studies conducted to determine the toxicity of sulphate in humans. Case reports of diarrhoea in three infants exposed to water containing sulphate at concentrations ranging from 630 to 1150 mg/L have been presented (Chien *et al*., 1968). However, the diarrhoea could not be explained as being solely due to exposure to high sulphate levels, and other factors may have played a role (e.g., consumption of infant formula with high osmolarity or the presence of microbial pathogens). A survey in North Dakota, USA, observed a slight increase in the percentage of people who reported a laxative effect when the drinking-water contained 500–1000 mg of sulphate per litre compared with people who reported a laxative effect with water containing <500 mg of sulphate per litre (28% versus 21%). Sixty-eight per cent of people consuming water with levels of sulphate between 1000 and 1500 mg/litre reported laxative effects. It was concluded that drinking water containing 750 mg of sulfate per litre was associated with a self-reported laxative effect, whereas water containing <600 mg/L was not. A reanalysis of the data found that most people experienced a laxative effect when they drank water containing >1000 mg of sulphate per litre (US EPA, 1999b).

Table 19: Sulphur contents in rocks and unconsolidated materials

| Material | S (ppm) |
|---|---|
| crust | 260 |
| Igneous rocks | |
| granite | 300 |
| basalt | 300 |
| Sediments | |
| shale | 2400 |
| sandstones | 240 |
| limestones | 1200 |
| Unconsolidated material | |
| alluvial | 100-1000's |
| shallow marine sediments | 1000-10000's |
| Coal | up to 10000' |

Source: Hitchon *et al*. (1999); Cox, 1995).

Table 20: Sources and mobilisation processes of sulphate

| Source/ process | Subsurface conditions | Natural environment | Anthropogenic / polluted environment |
|---|---|---|---|
| dissolution of sulphate minerals | | limestone aquifers;<br>evaporite deposits | |
| oxidative dissolution of sulphides | aerobic | young sandy;<br>aquifers;<br>mineralised areas | mining areas;<br>processing plants |
| sulphate leaching from surface | no specific environment | | unconfined quifers below fertilised soils |
| $SO_2$ uptake | no specific environment | uptake of fumarole gases | |
| acid rain | no specific environment | | industrialised areas |

Source: van Helvoort *et al*, 2006-2007).

Table 21: Sinks and immobilisation processes of sulphate

| Sink/ process | Subsurface conditions | Natural environment | Anthropogenic / polluted environment |
|---|---|---|---|
| sulphide precipitation | sulphate reducing | highly reducing aquifers rich in organic matter | |
| gypsum precipitation | no specific environment | evaporite deposits | mining areas |

**Phosphorus (Phosphates)**

Phosphorous is a multivalent nonmetal of the nitrogen group. It is found in nature in several allotropic forms, and is an essential element for the life of organisms. Phosphorus is the eleventh most abundant mineral in the earth's crust and does not exist in a gaseous state. Phosphates ($PO_4^{3-}$) are formed from the element phosphorus. Phosphates exist in three forms:

(i) orthophosphates: are produced by natural processes such as decay and are found in sewage. This very useful form of phosphorus is the one used by plants and animals for growth.

(ii) polyphosphate: are used for treating boiler waters and are found in many household detergents and soaps. In water, they change into the orthophosphate form.

(iii) Organic phosphates: are important in nature. Their occurrence may result from the breakdown of organic pesticides, which contain phosphates. They may exist in solution, as particles, loose fragments or in the bodies of aquatic organisms. (Osmond *et al*, 1995)

Phosphate is usually not readily available for uptake in soils. Phosphate is only freely soluble in acid solutions and under reducing conditions. In the soil it is rapidly immobilized as calcium or iron phosphates. Most of the phosphorus in soils is adsorbed to soil particles or incorporated into organic matter ( Holtan *et al.*, 1988). Phosphorus in aquatic systems occurs as organic phosphate and inorganic phosphate. Organic phosphate consists of a phosphate molecule associated with a carbon-based molecule, as in plant or animal tissue. Phosphate that is not associated with organic material is inorganic. Inorganic phosphorus is the form required by plants. Animals can use either organic or inorganic phosphate. Both organic and inorganic phosphorus can either be dissolved in the water or suspended (attached to particles in the water column) (US EPA, 2012).

### Sources of Phosphorus

(a). Nonpoint sources:

Natural: Phosphate deposits and phosphate-rich rocks release phosphorus during weathering, erosion, and leaching. Phosphorus may be released from lake and reservoir bottom sediments during seasonal overturns. Weathering of certain minerals, particularly apatite, provides a natural source of dissolved phosphorus in groundwater (Hitchon *et el*, 1999). Fluoroapatite provides the most extensively mined deposits. Phosphorus is strongly adsorbed to most sediments, and is capable of combining with a number of cations, particularly iron, aluminium, manganese and calcium, to form minerals that are stable in low-temperature aqueous environments (Robertson *et al*, 1998). However higher pH values (Lijklema, 1980; Detenbeck & Brezonik, 1991; Fox & Malati, 1993; Beauchemin *et al*, 1996) and more reducing conditions (Lijklema, 1980) tend to decrease a soil's ability to adsorb phosphate.

(b). Point sources:

Anthropogenic: The primary anthropogenic nonpoint sources of phosphorus include runoff from:

(i) land areas being mined for phosphate deposits,

(ii) agricultural areas, and

(iii) urban/residential areas.

Because phosphorus has a strong affinity for soil, little dissolved phosphorus will be transported in runoff. Instead, the eroded sediments from mining and agricultural areas carry the adsorbed phosphorus to the water body. An additional source is the overboard discharge of phosphorus-containing sewage by boats. Sewage treatment plants provide most of the available phosphorus to surface water bodies. Additional phosphorus originates from the use of industrial products, such as toothpaste, detergents, pharmaceuticals, and food-treating compounds. Primary treatment removes only 10% of the phosphorus in the waste stream; secondary treatment removes only 30%. The remainder is discharged to the water body. Tertiary treatment is required to remove additional phosphorus from the water. The amount of additional phosphorus that can be removed varies with the success of the treatment technologies used. Available technologies include biological removal and chemical precipitation (Tchobanoglous, 1991).

Phosphorus (P) is an essential nutrient for all life forms. Phosphorus plays a role in deoxyribonucleic acid (DNA), ribonucleic acid (RNA), adenosine diphosphate (ADP), and adenosine triphosphate (ATP). Phosphates for potable water treatment perform several functions that include: iron and manganese control, scale inhibition and removal, corrosion control and chlorine stabilization.

**Phosphorous in the environment**

(a) Environmental Effects: The growth of macrophytes and phytoplankton is stimulated principally by nutrients such as phosphorus and nitrogen. Nutrient-stimulated primary production is of most concern in lakes and estuaries, because primary production in flowing water is thought to be controlled by physical factors, such as light penetration, timing of flow, and type of substrate available, instead of by nutrients (McCabe *et al.*, 1985).

(b) Freshwater system impacts: Generally, phosphorus (as orthophosphate) is the limiting nutrient in freshwater aquatic systems. That is, if all phosphorus is used, plant growth will cease, no matter how much nitrogen is available. The natural background levels of total phosphorus are generally less than 0.03 mg/l. The natural levels of orthophosphate usually range from 0.005 to 0.05 mg/l (Dunne & Leopold, 1978). Many bodies of freshwater are currently experiencing influxes of phosphorus and nitrogen from outside sources. The increasing concentration of available phosphorus allows plants to assimilate more nitrogen before the phosphorus is depleted. Thus, if sufficient phosphorus is available, elevated concentrations of nitrates will lead to algal blooms. Although levels of 0.08 to 0.10 mg/l orthophosphate may trigger periodic blooms, long-term eutrophication will usually be prevented if total phosphorus levels and orthophosphate levels are below 0.5 mg/l and 0.05 mg/l, respectively (Dunne & Leopold, 1978).

(c) Freshwater systems: Nutrient-induced production of aquatic plants in freshwater has several detrimental consequences:

(i) Algal mats, decaying algal clumps, odors and discoloration of the water will interfere with recreational and aesthetic water uses.

(ii) Extensive growth of rooted aquatic macrophytes will interfere with navigation, aeration, and channel capacity.

(iii) Dead macrophytes and phytoplankton settle to the bottom of a water body, stimulating microbial breakdown processes that require oxygen. Eventually, oxygen will be depleted.

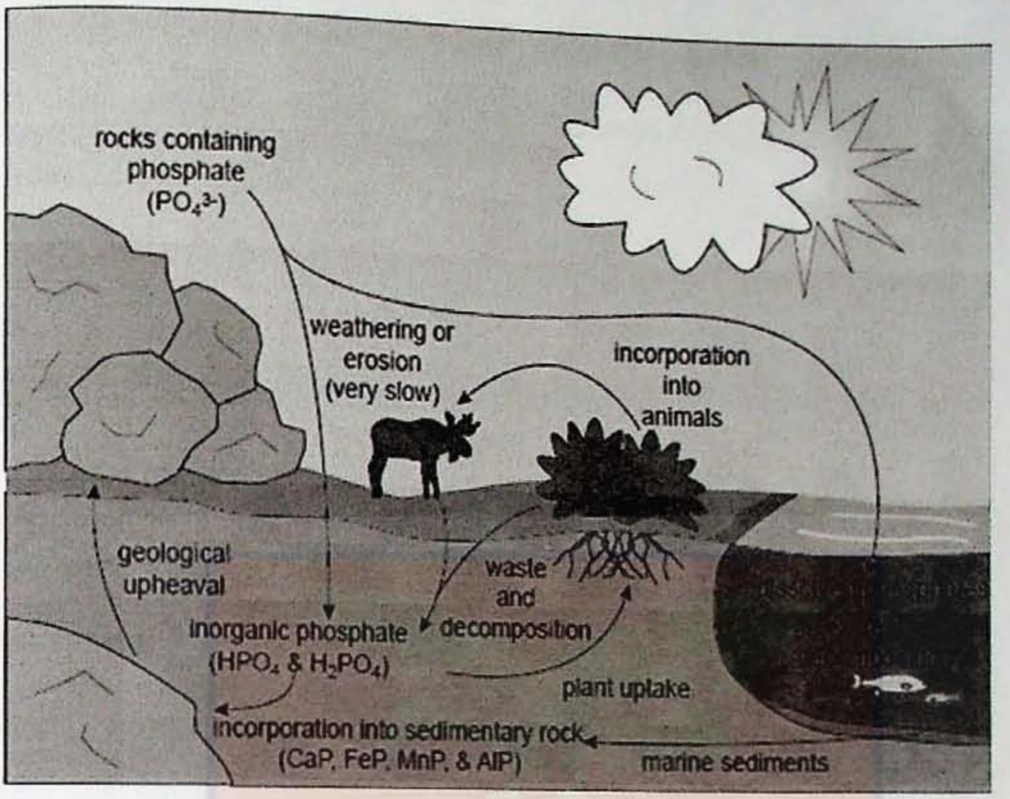

Figure 15: The Phosphorus Cycle in Ecology (Enger & Bradley, 2002)

(iv) Aquatic life uses may be hampered when the entire water body experiences daily fluctuations in dissolved oxygen levels as a result of plant respiration at night. Extreme oxygen depletion can lead to death of desirable fish species.

(v) Siliceous diatoms and filamentous algae may clog water treatment plant filters and result in reduced time between backwashing (process of reversing water flow through the water filter in order to remove debris).

(vi) Toxic algae (occurrence of "red tide") have been associated with eutrophication in coastal regions and may result in paralytic shellfish poisoning.

(vii) Algal blooms shade submersed aquatic vegetation, reducing or eliminating photosynthesis and productivity (Dennison *et al.*, 1993; Batiuk *et al.*, 1992).

Table 22: Some applications of Phosphorus

| **Widely used compounds** | **Use** |
|---|---|
| $Ca(H_2PO_4)_2 \cdot H_2O$ | Baking powder and fertilizers |
| $CaHPO_4 \cdot 2H_2O$ | Animal food additive, toothpowder |
| $H_3PO_4$ | Manufacture of phosphate fertilizers |
| $PCl_3$ | Manufacture of $POCl_3$ and pesticides |
| $POCl_3$ | Manufacturing plasticizer |
| $P_4S_{10}$ | Manufacturing of additives and pesticides |
| $Na_5P_3O_{10}$ | Detergents |

## Previous Works

Several studies have used a combination of environmental tracers (e. g. major ions, stable and radioactive isotopes) to assess groundwater-surface water interactions (Crandall *et al*, 1999; McCarthy *et al*, 1992; Herczeg *et al*, 2001; Cook *et al*, 2003; Baskaran *et al*, 2004).

Hydrochemical and stable isotope ($^{18}O$ and $^{2}H$), analyses of groundwater samples were used by Kortatsi (2007) to establish the hydrochemistry of groundwater in the Ankobra Basin, which is to the western side of the study area. The groundwater was said to be generally mildly acidic, low in conductivity and undersaturated with respect to carbonate phases. Major ions except bicarbonate were low and dissolved silica was moderately high. Approximately, 20%, 5%, 40% and 25% respectively of boreholes had aluminium, arsenic, iron and manganese concentrations exceeding the respective WHO maximum acceptable limits for drinking water. The relatively large percentage of boreholes with high concentration of aluminium reflects the acidic nature of the groundwater.

Another work by Kortatsi *et al* (2007) on the Hydrogeochemical evaluation of groundwater in the lower Offin basin, Ghana analysed boreholes, dug wells, springs and mine drainage samples for major ions, minor and trace elements. Major ion study results show that the groundwater is, principally, Ca–Mg–$HCO_3$ or Na–Mg–Ca–$HCO_3$ in character, mildly acidic and low in conductivity. Approximately 19 and 46% of the boreholes have arsenic and iron concentrations exceeding the WHO's Guidelines for drinking water quality.

Fianko *et al* (2007) also combined isotopic and hydrochemical characteristics of samples in the Densu River Basin to show the influence of natural and anthropogenic sources of nutrients in the basin. The results of the study indicated gross pollution of the Densu River with respect to nutrients and organic matter. Karikari *et al* earlier, conducted a water quality assessment in the Densu Basin of Ghana between July 2003 and March 2004 and identified human, animal and agricultural activities as the main sources of groundwater in the Ankobra Basin, which is to the western side of the study area. The groundwater was said to be generally mildly acidic, low in conductivity and undersaturated with respect to carbonate phases. Major ions except bicarbonate were low and dissolved silica was moderately high. Approximately, 20%, 5%, 40% and 25% respectively of boreholes had aluminium, arsenic, iron and manganese concentrations exceeding the respective WHO maximum acceptable limits for drinking water. The relatively large percentage of boreholes with high concentration of aluminium reflects the acidic nature of the groundwater.

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# CHAPTER THREE

# METHODOLOGY

## Study Area

The study area is located in the Central Region, which is one of the 10 administrative regions of Ghana. The Ayensu river Basin transverses the Awutu-Senya, Gomoa East, and Agona East districts. The Ayensu River takes its source from the Bunsu Hills, an extension of Atewa Range, North of Asamankese, from where it flows generally southward to the sea near Winneba. River Ayensu has been dammed at Gyehadze for the Winneba water supply system and Kwanyarko for the Kwanyarko Water Supply system.

The study area is located in the Central Region of Ghana (Fig. 16 and 17). The area covers approximately 1,709 km$^2$ and lies between latitudes 5$^{\circ}$ 150'N - 6$^{\circ}$ 00'N and longitudes 0$^{\circ}$ 300'W - 0$^{\circ}$ 450'W. The river drains into the sea through the Muni and Oyibi lagoons. The Ayensu Basin is bounded on the east by the western boundary of the Densu Basin, on the north by the southeastern boundary of the Pra Basin, on the west by the eastern boundary of the Ochi-Nakwa Basin, on the south by the Gulf of Guinea. The Ayensu and its principal tributaries, mainly the Akron, Abuchem, Ansum and the Suwurum drain an approximate area of 1,709 km$^2$ (WRMS, 2008).

The Ayensu river is one of the main rivers in the Central Region of Ghana. The river basin is an important agricultural area, and the alternation of rainy and dry periods affects the economy of the population. The catchment is drained by a series of streams with a general trend of north –south direction. The area stretches from the Coastal Savanna Grassland through woodland to the Semi-Deciduous Rain-Forest Zone of the Humid Forest Region of Ghana where rainfall and humidity are quite high. It has an equatorial monsoon type of climate characterized generally by two rainy seasons with monthly totals reaching their maxima in May-June and October. Yearly average total rainfall varies from1270 to 1600mm (WRMS, 2008).

### Relief (Topography)

The Ayensu Basin is an area of dissected and diversified relief from the coast to the upper reaches where Atewa ranges from the highest elevations at 615 metres above sea level. The relief consists of steep mountain lands, hilly lands and rolling lands and a coastal plain with slopes ranging from 0 – 2% at the coast to 30% inland. Generally, the topography is subdued towards the coastal south where elevations range between 30 and 60m above mean sea level (WRMS, 2008).

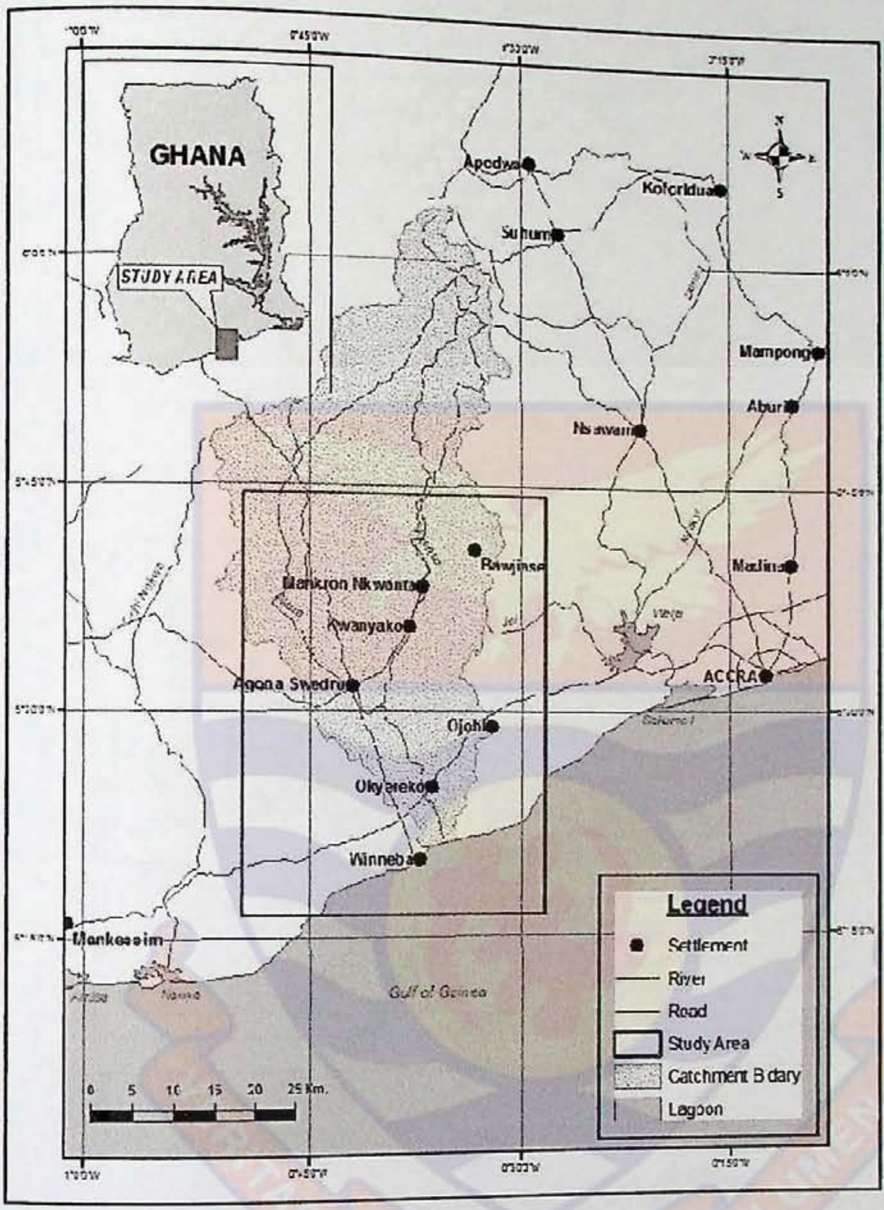

Figure 16: Location map of the study area

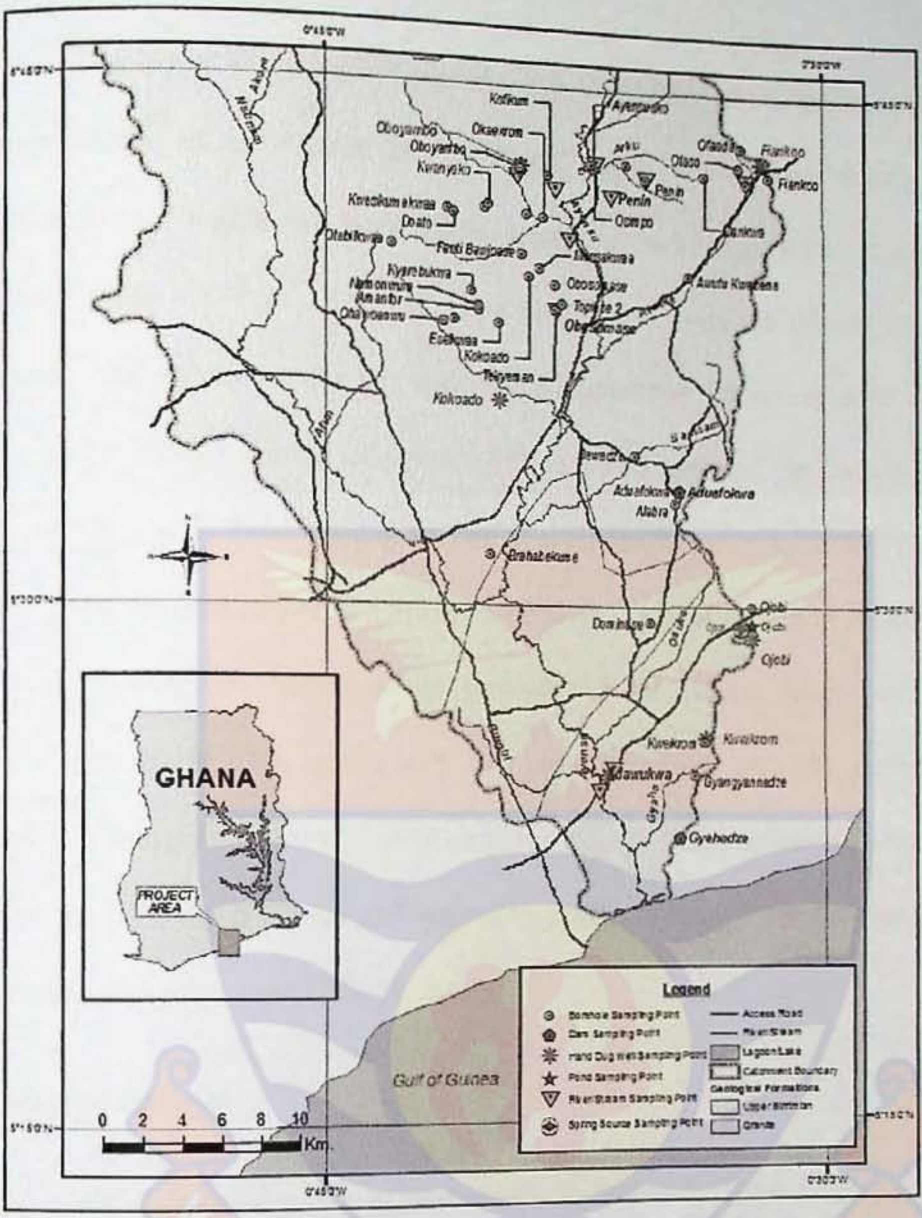

Figure 17: Map showing the catchment areas of the Ayensu River and the sampling sites

## Climate and Vegetation

The basin has a varied climatic and vegetation characteristics. The upper reaches of the Ayensu fall within the moist (humid) semi-deciduous rainforest zone with a two peak rainfall regime of an average annual rainfall ranging from 1,370 to 1,650 mm. The central and southern coastal areas, however fall within the dry marginal Forest- Savannah Transition zone with an average annual rainfall of some 1,145 to 1,650 mm and the Sub-humid Coastal Savannah Zone with an annual average rainfall ranging from 750 to 1,150 mm, respectively. The original vegetation cover of the basin consisted of moist evergreen forest at the summits of the Atewa ranges in the headwaters areas. The moist and dry semi-deciduous and the marginal transition forest in the middle basin traverses through to the coastal sub-humid savannah with scrub thicket and grasses to patches of mangrove swamps and wetlands along the coast (WRCS, 2008).

## Geology and Soils

The Ayensu Basin is predominantly underlain by Cape Coast granite complex consisting largely of granites, schists and gneisses which has resulted in the occurrence of such soil groups as Forest and Savannah Ochrosols, and Forest and Savannah Lithosols on the uplands and Forest and Savannah Gleisols within the valley bottoms.

There are however, small areas within the northwest and southwest (Winneba area) underlain by upper Birimian basic rocks which give rise to the occurrence of Savannah Ochrosol- Rubrisol Intergrades and Tropical Black Clays. Saline soils of the Sodium Vleisols group also occur along the banks of the Muni lagoon near Winneba. Within the northeastern and southeastern sections, there are limited areas underlain by metamorphosed sediments of the Togo and Voltaian systems consisting mainly of quartzites, sandstones, and conglomerates. Such areas are also occupied by soil groups similar to those occurring within Cape Coast granitic areas. The rest of the soil groups occurring within the Ayensu basin, namely. Forest Ochrosols, Forest Lithosols, Forest Greisols, Savannah Ochrosol-Rubrisol Intergrates and Tropical Black Clays are described as follows ( WRCS, 2008):-

### Forest Ochrosols (Acrisols, Lixisols)

Forest Ochrosols are by far the most extensive soils in the Semi-Deciduous Rain Forest Zone. They cover some 30,506Km$^2$ within the forest region of the country. Typical Forest Ochrosols are mainly red and well-drained on the upper slopes and brown and moderately well drained on the middle slopes and developed over or in the weathering products of moderately acid rocks. Textures vary from moderately heavy to light depending upon the prevailing geological rock. Such soils have marked concentration of organic matter in the upper A horizon with strongly leached lower horizons. Typical soil profile reaction ranges from near- neutral (pH 6.7 – 6.9) in the topsoil becoming slightly to moderately acid (pH 5.5 -6.5) with depth. The cation exchange capacity (CEC) is less than 15 m.e. per 100 gm soil throughout the profile and base saturation is more than 50% in the A horizon but less in lower horizons. An argillic B- horizon is present and the predominant clay mineral is kaolinite with considerable amount of iron, aluminium and manganese.

### Forest Lithosols (Leptosols)

Forest Lithosols are immaturely developed soils occurring on high ranges with steep slopes. They are very shallow, mainly excessively well-drained soils directly over incompletely weathered and/or hard rock. They are subject to severe to very severe erosion hazard and must therefore be kept permanently under forest vegetation in order to protect existing watersheds. They cover an area of about 5,586Km$^2$ within the forest zones of the country.

### Forest Gleisols (Dystric and Eutric Gleisols)

Forest Gleisols are predominantly, very deep to deep, grey imperfectly to very poorly drained alluvial soils developed in soil materials transported from up-slope and deposited in the valley bottoms. Such soils are often mottled with depth and usually become waterlogged during the main rainy season.

### Savannah Ochrosol – Rubrisol Intergrates (Nitisols)

They are very limited in extent within the savannah zones of the country covering some 776 km$^2$. They consist mainly of either, well to moderately well-drained, reddish brown, non-gravelly, heavy to moderately heavy clays over basic rocks on flat summits. They are moderately deep to moderately shallow, moderately to imperfectly drained, red, brown and olive mottled concretionary sandy clays over basic intrusive rocks. Such soils are inherently very fertile with good physical conditions making them the most productive soils within the savannah zones of the country.

### Tropical Black Clays (vertisols)

Tropical Black Clays are dark coloured, heavy, alkaline, cracking clays occurring over level to near-level gilgai micro-relief. They cover approximately 2,141km$^2$ within the savannah zones of the country. Clay content of the soils is more than 30% and base saturation is more than 50% throughout the profiles. Organic matter is generally less than 4% in the A horizon. The pH is near neutral at the surface (6.6- 6.9) becoming increasingly alkaline with depth. Such soils become saturated with water during the peak of the rainy season and dry out almost completely developing wide cracks during the dry season (WRMS, 2008).

## Hydrometeorology

### Rainfall

The Ayensu Basin experiences two rainy seasons – major and minor. The major rainy seasons occur between April and July, with the peak in June. This is followed by a short dry spell in August. The minor season occurs between September and October followed by a longer dry spell from December to March. The mean annual rainfall in the Ayensu Basin Varies from 845mm – 1150mm in the Southern Coastal part of the basin to about 1370mm – 1650mm in the upper reaches of the basin. The mean monthly rainfall shows a wide variation. In terms of water supply, within the critical dry months of December to February, the mean monthly rainfall values around Kwanyaku range from 22mm to 29mm. In the non – critical months, it ranges from 72.9mm to 202.8mm in the same vicinity.

### Temperature

The mean annual temperature recorded around Winneba and Efutu Awutu Senya is 26.3°C with a diurnal variation of 3 °C - 4 °C. The mean monthly values range from 24.3 °C in August to 28 °C in January, February, and March ( WRMS, 2008; Dankwa, 1974; Danida, 1994).

### Relative Humidity

The mean annual relative humidity for the Winneba/Efutu Awutu Senya area is 87%, with corresponding minimum relative values of 78% and 96% respectively. The mean monthly minimum relative humidity varies between 68% and 81%. The mean monthly maximum relative humidity ranges from 93% - 96%. (GWC Ltd, 2010)

### Land Use

The basin area north of the coastal savannas was part of the early cocoa growing areas in the country in the first half of the present century. Most of the forest was opened up for cocoa cultivation, which is currently replaced by intensive bush fallow food crop cultivation (cocoyam, plantains, cassava, maize, vegetables) and oil palm plantation development. The original forest cover is almost completely eliminated. What is left is the forest reserve on part of the Atewa ranges. The present cover consists of small areas of secondary forest with low bush fallow regrowth in the forest areas and grasses in the coastal zone. There is little forest remaining except the reserved forests at the summits of the Atewa ranges. Large numbers of cattle are known to be kept on the coastal plains while coconut plantations occur behind the beaches.

The land use categories mapped by the Remote sensing Applications Unit include mixed bush fallow food cropping with thicket and grass grazing in the south to intensive bush fallow food cropping, and sub-canopy cropping with cocoa (RSAU, 19995).

## METHOD

The methodology employed in this work comprised of a desk study, field study, quality assurance and then data processing and presentation. The flow diagram for the procedure adopted in this work is presented in Fig. 18.

## DESK STUDY

From December 2009 various organizations were visited to collect relevant information on climatic data, water resources, water supply facilities, topographic map sheets, drilling reports and water quality data. The desk study included the acquisition and review of all relevant reports, other documents and papers and existing data of the study area. Topographic data (both hard copy and digital), geological, hydrological and hydrogeological maps and lithologic sections were obtained from the Survey Department, Ghana Geological Services and the Community Water and Sanitation Agency (CWSA) in the Central Region. The borehole logs, borehole location map, water quality data and geochemical data of the rocks in the study area were gathered from the Baseline Study of Hydrogeology and Water Resources in Central Region Volume 1, Technical Report Prepared for CWSA, Central Region by Water Resources Consultancy Services Limited.

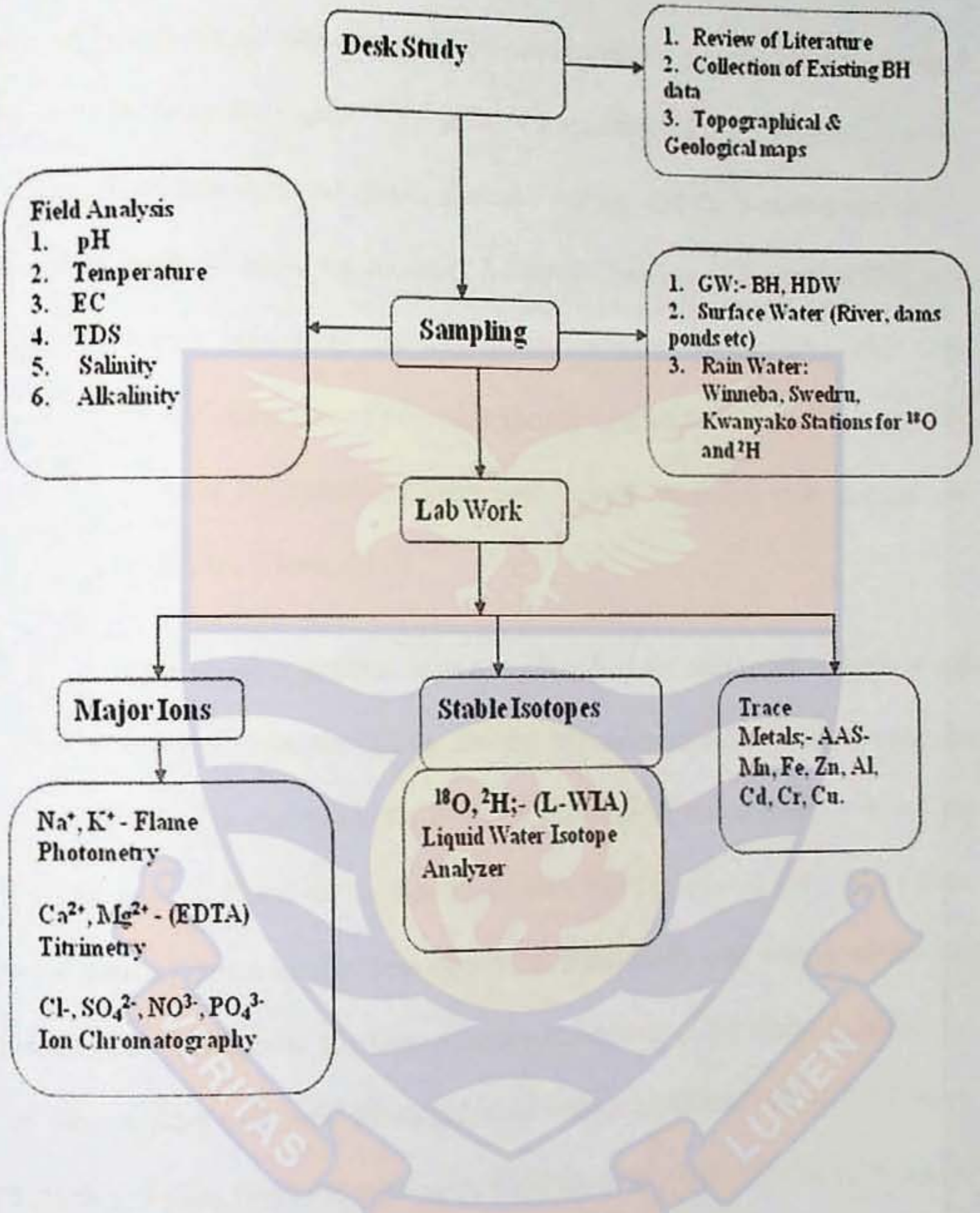

Figure 18: Flow diagram for the procedure adopted in this work

## Fieldwork

The initial process began with a visit to the various communities for physical inspection of the facilities (boreholes, handdug wells etc), those in use and the broken down ones and new ones available outside the list provided by the CWSA in the region. The facilities were selected from the southern part of the river basin (near the coast), the mid- portion and the northern end where most of the bore holes are located. A Global Positioning System (GPS) was used to locate accurately the coordinates of each sample site. The GPS coordinates and elevation of the water facility was taken, the facility type was also taken. GPS localizations of the water supply facilities were carried out using a GARMIN ETrex, GPS.

Three weather stations were also identified for rain water sampling and other weather parameters. These are the Winneba weather station, near the coast, Swedru in the mid-portion and Kwanyako in the northern part of the Central region. Some of the boreholes with hand pumps in the project area, were broken down at the time of the field inventory and others which had broken down had been abandoned during the course of the study. In all a total of 64 sampling sites were identified; these included 7 hand dug wells, 2 dams, 1 spring, 9 sites from the main river (Ayensu river) and its tributaries and 45 boreholes with hand pumps. During the course of the studies 5 boreholes broke down but were sampled in some of the campaigns. The sampling sites were selected to cover the entire Ayensu basin in the central region; i.e. the southern coastal portion, the middle zone and the northern portion where most of the boreholes are located.

## SAMPLE COLLECTION

Water samples were collected from 14th January, 2010 in the dry season and 10th January 2012. Groundwater samples were collected following the sample protocol for groundwater sampling set out by Weaver (1992).The water samples were collected in 500 mL acid-washed high density polyethylene sampling bottles after filtering through 0.45μm filters on cellulose acetate with a hand operated vacuum pump. (Cellulose Nitrate Filter from Sartorius AG Goettingen, Germany). The filtered water samples for metal analysis were acidified with 1% $HNO_3$ to keep metals in solution. The water samples were analyzed in the field for temperature, pH, electrical conductivity (EC), total dissolved solids (TDS) and salinity using pH/conductivity meter (CyberScan PC6000) with a glass electrode (APHA, 2004).

The rainwater samples were collected following IAEA Technical Procedure for Precipitation sampling for Isotopic Analysis. The rain water is collected in the standard rain gauge which is read and emptied after each rain event. The rainwater is then poured into a 1½ litre polyethylene bottle with a cap. The bottle was tightly closed to avoid evaporation and kept in a cool dry place. The rainwater samples were filled into 50 mL bottles supplied by IAEA and sent to laboratories of the Nuclear Chemistry and Environmental Research Centre, National Nuclear Research Institute, Ghana Atomic Energy Commission, Kwabenya, Accra, for deuterium and oxygen-18 analysis.

Figure 19: Photograph of sampling site of the dam at Gyehadze for the Winneba Water Project.

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Figure 20: Photograph of the spring at Ojobi

Figure 21: Photograph of the hand dug well at Kweikrom.

Figure 22: Photograph of the inside of a hand dug well in the dry season.

Figure 23: Photograph of a foot operated pump fitted to a Borehole.

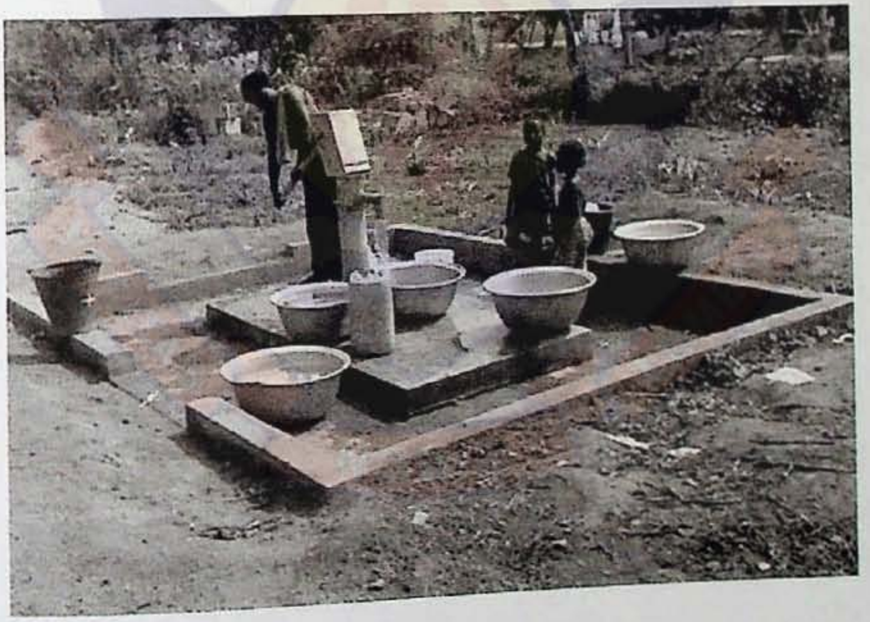

Figure 24: Photograph of a hand operated pump attached to a Borehole.

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Figure 25: Photograph of another example of hand operated pump attached to a Borehole.

Figure 26: Photograph of sampling water from the Ayensu river at Kwakwa.

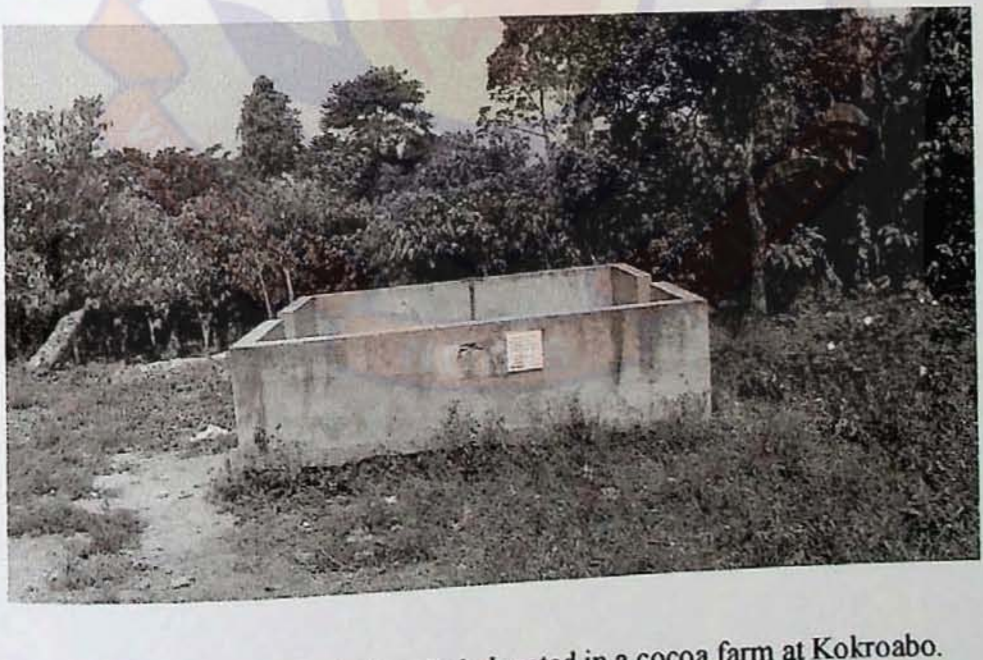

Figure 27: Photograph of a borehole located in a cocoa farm at Kokroabo.

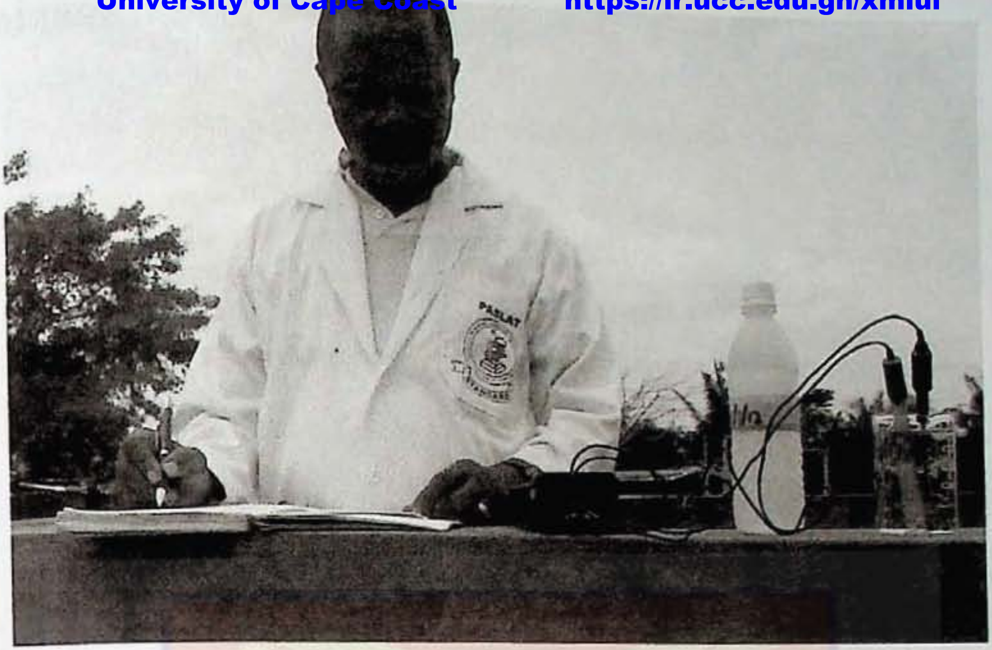

Figure 28: Photograph of pH, TDS and conductivity determination in the field using a portable meter.

## PHYSICAL ANALYSIS

The pH, electrical conductivity (EC), total dissolved solids (TDS) and temperature were determined in the field using CyberScan PC6000 pH/conductivity meter and later the HACH sensION™ + Portable Meter. The CyberScan PC6000 meter has different probes for the conductivity, temperature and pH but the HACH sensION™ + Portable Meter uses the same probe to measure EC, TDS, pH and temperature.

## CALIBRATION OF THE HACH senION$^{TM}$ + PORTABLE METER

The probe is a combination gel-filled electrode with a built-in temperature sensor for pH and conductivity measurements. It has a Ag/AgCl reference electrode with a range of 0 to 14 pH and 5μS/cm to 30mS/cm conductivity. The procedure followed for the calibration was as outlined in the manufacturer's user manual. The electrode was connected to the meter and calibrated using pH of 4.01 and 10.01 at 25°C according to the manufacturer's procedure for two calibration standards. The values for the electrical conductivity are 1413 μS/cm and 12.88 mS/cm at 25°C.

The buffers and calibration solutions were poured into the labelled calibration tubes provided. The probe was rinsed with deionized water and put into the first calibration tube. Care was taken so that no air bubbles are left under tip of the probe. The calibration key was pushed to select the parameter (pH) and pushed again to measure the first calibration solution. The probe was again rinsed with deionized water, put into the second calibration tube and the key was pushed again to measure the second calibration solution. The probe was rinsed with deionized water and the same procedure as outlined above was repeated for the calibration of the electrical conductivity (EC)

### Alkalinity Measurement

The method of potentiometric titration to a preselected pH, as set out in Standard Methods (2005), was used for the alkalinity measurements. Alkalinity titrations were carried out at the sampling sites with 0.16 N $H_2SO_4$

using HACH Digital Titrator Model 16900. All the reagents and the indicators are suplied by the manufacturer ( Hach Company, U. S. A.).

All water samples were transported to the laboratory in ice-filled coolers, and kept refrigerated at approximately 4° C until analysis.

Figure 29: Photograph of Alkalinity titration in the field using HACH Digital Titrator Model 16900.

Figure 30: Photograph of filtering water samples in the field using hand operated vacuum pump.

## LABORATORY WORK (CHEMICAL ANALYSIS)

Water samples collected were analyzed by both classical and automated instrumental methods prescribed by the standard methods for the analyses of water and wastewater and EPA (Standard methods 2004; EPA, 1983).

## DETERMINATION OF TOTAL HARDNESS (EDTA TITRIMETRIC METHOD)

Reagents:

1. Standard EDTA titrant (0.01M)
2. Eriochrome BlackT indicator
3. $NH_3$/ $NH_4Cl$ buffer solution
4. Standard calcium solution (1000mg/L)

All reagents are analytical grade reagents from Sigma-Aldrich chemie GmbH, Germany.

(a) Standardization of EDTA solution

A 20.0 mL sample of the calcium standard solution was pipetted into a 250 mL conical flask and diluted to 100 mL with deionised water. To this solution 4 mL of $NH_3$ / $NH_4Cl$ buffer solution and 6 drops of the Eriochrome black T indicator solution were added to produce a claret colour and a pH of 10.0. This solution is then titrated with the EDTA solution until the colour of the solution changed from wine red to a distinct blue end-point.

$$E\,(CaCO_3) = \frac{20 \times 1\ mg\ (CaCO_3).}{t}$$

where

E = mg $CaCO_3$ equivalent 1mL of EDTA titrant =1mg$CaCO_3$

t = volume of EDTA used

(b) Procedure for determination of Total hardness:

A 50.0 mL sample of each of the water samples was pipetted into a 250 mL conical flask and 4 mL of the pH 10 $NH_3$ / $NH_4Cl$ buffer solution and 6 drops of Eriochrome black "T" indicator were added to each flask. The resulting solution was then titrated with standard 0.01M EDTA until the colour of the analyte changed from wine red to blue. This procedure was repeated and two consistent titre values were averaged ($V_1$) and used to calculate the concentration.

$$\text{CaCO}_3 \text{ content (in mg/L)} = \frac{V_1 \times E\,(\text{CaCO}_3) \times 1000}{50}$$

## DETERMINATION OF CALCIUM (EDTA TITRIMETRIC METHOD)

Reagents:

1. Standard EDTA titrant (0.01 M)
2. 2M NaOH solution
3. Murexide indicator

Procedure:

A 50.0 mL sample each of the water samples was pipetted into a 250 mL conical flask and then 2 mL of 2M NaOH solution and a pinch of murexide indicator were added and swirled for the indicator to dissolve and for complete precipitation of $Mg(OH)_2$. The solution was titrated against 0.01M standard EDTA until the pink colour changes to bluish violet. The titre values were recorded and the calcium concentration was calculated using the average value (V) of two consistent titre values.

$$\text{CaCO}_3 \text{ content (in mg/L)} = \frac{V \times E\,(\text{CaCO}_3) \times 1000}{50}$$

## DETERMINATION OF MAGNESIUM (CALCULATION METHOD)

The magnesium present in the water sample was calculated by subtracting the volume of EDTA solution required for the calcium determination from the volume required for the total hardness determination for equal volumes of the sample ($V_1$-V).

$$\text{CaCO}_3 \text{ content (in mg/L)} = \frac{(V_1 - V) \times E\,(\text{CaCO}_3) \times 1000}{50}$$

## DETERMINATION OF CHLORIDE (MOHR'S METHOD)

Reagents: All reagents are Analytical grade reagents from Sigma-Aldrich chemie GmbH, Germany.

1. 5% $K_2CrO_4$ indicator solution
2. 0.01M standard $AgNO_3$ solution

Procedure:

A 10.0 mL sample of each water sample was pipetted into a conical flask and 1mL of $K_2CrO_4$ solution added to obtain a yellow coloured solution. The titrant, Silver nitrate solution was first standardized against sodium chloride primary standard. In order to adjust the pH of the solutions, small quantities of $NaHCO_3$ were added until effervescence ceased. The 0.01M $AgNO_3$ was run from the burette until the first permanent appearance of red $Ag_2CrO_4$. A blank determination was carried out using distilled water.

$$\text{Chloride content (in mg/L)} = \frac{C \times V \times M(Cl^-) \times 1000}{\text{Volume of Sample Used}}$$

Where C = concentration of $AgNO_3$Titrant used.

V = Volume of $AgNO_3$ Titrant used.

$M(Cl^-)$ = Molar mass of Cl

## DETERMINATION OF ANIONS ($SO_4^{2-}$, $Cl^-$, $NO_3^-$, AND $PO_4^{3-}$) (Ion chromatography Method)

In this work the Dionex ICS - 900 Ion chromatography System in conjunction with a conductivity detector was used to determine the anions present from the water samples in the Ayensu River Basin (EPA, 1993 ; Dionex, 2004).

### Reagent and Standard

1. Eluent: Sodium carbonate (0.8 mM)/ sodium hydrogencarbonate (0.1mM)
2. Seven anion Sandard II (combined standard supplied by the manufacturer).

| | |
|---|---|
| Column: | Dionex IonPac AS24, 2mm |
| Flow rate: | 0.3mL/min |
| Injection volume: | 2.5μL |
| Detection: | Suppressed conductivity<br>Dionex AMMS 300,2mm |

Procedure:

When the standard was run all the peaks of the anions ($Cl^-$, $SO_4^{2-}$, $NO_3^-$, and $PO_4^{3-}$ ) appear. The filtered water samples obtained from various locations were then analyzed. Sample solutions pass through a pressurized chromatographic column where ions are absorbed by column constituents. The pump forces the eluent to pass through the separator columns where the ions were separated by ion-exchange. The conductivity cell transmits the signal to a computer running a chromatography software. The software identifies ions based on retention time and quantifies each analyte by integrating the peak areas. The results were displayed as a chromatograph with the concentration of ionic analytes automatically determined and tabulated.

## DETERMINATION OF TRACE METALS (Zn, Cu, Cd, Cr, Mn, Fe and Al)

The standard method for determining trace concentrations of soluble heavy metals began with filtering through 0.45µm pore diameter cellulose Nitrate membrane filter after which the filtrate was preserved with concentrated $HNO_3$. The water samples were then analysed by Flame Atomic Absorption Spectrometry (APHA, 2005) using VARIAN AA240FS Atomic Absorption Spectrometer (AAS) - fast sequential in an acetylene-air flame. The AAS was calibrated with relevant analytical grade standards.

Reference standards used are from FLUKA ANALYTICAL, Sigma-Aldrich Chemie GmbH and product of Switzerland. The following Quality Control and Quality Assurance techniques were used during the analysis:

BLANKS: They were to check contamination during sample preparation.

DUPLICATES: To check the reproducibility of the method used.

STANDARDS: to check the efficiency of the equipment being used.

**PROCEDURE**

1. The acidified samples were digested to break away compounds that are bound together to allow only metals in solution.
2. Each metal to be analyzed for had a characteristic lamp that was replaced from time to time.
3. Each water sample was aspirated through a compartment to the flame chamber to be atomized.
4. The heating temperature used ranged from 800-1800 degree celsius, from metal one to seven.
5. Metals were heated at required temperatures e.g. (aluminium at a temperature of 1200°C) that atomized metals could only absorb radiation from the lamp.
6. The various wavelengths at which radiations were absorbed from the lamps were 309.3 for aluminium, 279.5 for manganese, 324.7 for copper, 248.3 for iron, 228.8 for cadmium, 357.9 for chromium and 213.9 for zinc.
7. The presence of a sample compartment accommodated the atom which had absorbed the radiation, hence was the radiation that was detected for.
8. The monochromator only allowed specific wavelength e.g. for Copper, 324.7 to pass through the detector.
9. The detector detected the radiations of specific wavelength that moved in from the monochromator.

10. The readout compartment of the Atomic Absorption Spectrometer (AAS) gave the various concentrations accurately.

## DETERMINATION OF SODIUM AND POTASIUM USING FLAME PHOTOMETRY

Flame photometry is used in determining Sodium and Potassium in water samples collected from the various sampling sites (Clesceri *et al*., 1998). The Sheerwood Model 420 Flame Photometer was used to determine the Sodium (Na) and Potasium (K) content of the water samples. Emission wavelength for Na is 589 nm and for K 766 nm.

The fuel used in the operation of the flame photometer is the Liquefied Petroleum Gas (LPG).

Components are aspirator, nebulizer, atomization chamber, a detector and a pump.

Reagents:

1. Lithium standard solution
2. Na/K Combined Standard (100ppm)
3. Deionized water

**Procedure:**

The instrument was calibrated with a Blank (deionized water) and one Standard (100ppm Na/K combined standard). A 2.0 $cm^3$ sample of Lithium standard solution was added to 5.0$cm^3$ of each water sample in a test tube and the mixture shaken to mix well. The lithium solution is a suppressant that prevents ionization of the atoms.

All Blank, Standards and sample solutions were introduced into the flame by aspiration. One end of small diameter tubing was placed into the sample cup. The other end of the tubing was attached to an Aspiration Needle. Compressed air was forced through a small orifice and past the tip of the needle. The high velocity of the air stream caused the solution to form an aerosol which entered the mixing chamber where it was mixed with the fuel gas (LGP) and larger droplets were excluded. The small droplets made their way to the flame (atomization chamber) where they underwent the excitation and emission processes. The flame photometer uses two channels; one for Na and the other for K. After every sample determination the system was flushed with deionized water before the next measurement. The results were read out from the display panel.

## DETERMINATION OF THE STABLE ISOTOPES ($^{2}$H AND $^{18}$O) USING LIQIUD-WATER ISOTOP ANALYZER.

The LOS GATOS Research (LGR) Liquid- Water Isotope Analyzer DLT - 100 was used in analyzing water samples from the Ayensu River basin for oxygen and hydrogen stable isotopes ($^{18}$O and $^{2}$H).

- The DLT-100 Liquid-Water Isotope Analyzer uses tunable, off-axis integrated-cavity laser spectroscopy developed by Los Gatos Research to measure hydrogen and oxygen isotopic composition ($\delta^{18}$O and $\delta^{2}$H) in liquid water samples.
- Precision is about 0.8 or less for $\delta^{2}$H and 0.3 or less for $\delta^{18}$O.

**Components**: Pump, analyzer, auto-sampler and Driente (fuel)

**Standards:**

(a) International Standards:-

1. Vienna standard mean ocean water (V-SMOW)
2. Green Ice Standard Precipitation (GISP)
3. Standard Light Antartic Precipitation (SLAP)

(b) In-house Standards

| | |
|---|---|
| Standard 1 | Water from high altitude |
| Standard 2 | Distilled sea water |
| Standard 3 | Control (Tap water) |

**Procedure:**

A 1mL aliquots of samples were used and 6 replicates were sequentially measured for each sample through an auto-injector. The first 3 measurements were discarded to eliminate memory effects, and the average of the last 3 measurements (#4-6) were used for isotope ratio calculations.

Working standard references calibrated against NIST standard reference materials (VSMOW, GISP, and SLAP) were dispersed in the sample sequence. Sample isotope ratios were converted to Del notation based on working standard references. They were all arranged according to the IAEA spread sheet for arranging standards and samples in the tray i.e. dummy first followed by standards 1, 2, 3 and 5 of the water samples. The same arrangement was followed until all the samples were exhausted with the dummy being placed last.

The auto-sampler was put on and then given the run command with six (6) injections per sample. After the first injection, the volume of the water molecules (2-4 x$10^{16}$) and the spectrum were checked before the analysis was continued. The LGR analyzer has an internal computer and software that automatically apply calibration standard measurements made during the sample run, to graphically display all results, and to diagnose instrument operation.

### Accuracy check on chemical analyses

### Charge Balance Error (CBE)%

The water quality results that were obtained from the laboratory were entered into an Excel spreadsheet and the ionic balance checked. All data with a balance outside 5% ratio of EPM Cation: EPM Anion Ratio is sent back to the lab for re-analysis. EPM means Equivalents Per Million. Normally a charge balance error of < 10% is considered to be acceptable.

The ionic balance was determined for the results of the major cations and anions and the results are presented in the table of analysis in Chapter 4. The ionic balance was calculated by:

$$CBE = \frac{C(mq/L) - A(meq/L)}{C(meq/L) + A(meq/L)} \times 100\%$$

where C = Cation A = Anion

## Correlation Coefficient

The hydrochemical parameters determined in the groundwater and surface water samples were entered into a Microsoft Excel spreadsheet and the different corellations determined.

Correlation coefficient is commonly used to measure and establish the relationship between two variables. It is a simplified statistical tool to show the degree of dependency of one variable to the other (Belkhiri *et al.*, 2010).

## Saturation Indices

The saturation indices were determined using the hydrogeochemical equilibrium model, Phreeqc for Windows (Parkhurst & Appelo, 1999).

The saturation index (SI) of groundwater samples with respect to mineral precipitation is expressed by:

$SI = \log_{10}(IAP/Ksp)$

where IAP is the ion activity of the solution and $Ksp$ is equilibrium constant which is the solubility product at a given temperature. The thermodynamic data used in this computation were those contained in the default database of the Phreeqc for Windows.

# CHAPTER FOUR

## RESULTS AND DISCUSSION

### RESULTS

The hydrochemical water quality parameters determined in gruondwater, surface water and rainwater samples in the Ayensu river basin by the various classical and instrumental standard methods are presented and discussed in this chapter.

A statistical summary of hydrochemical parameters measured in the 60 water samples (groundwater and surface) is presented in Tables 23 and 24 and the actual results are presented in appendices 1 and 2.

### DISCUSSION

The data collected over the study period were compared to the guidelines for groundwater set by WHO for domestic purposes as shown in tables 23 and 24. From the results, very wide ranges and high standard deviations are easily recognized for most of the parameters. Such wide ranges for solute concentrations suggest that multiple sources and/or complex hydrochemical process take place to generate the chemical composition. The large variations in mean, median and standard deviation values of ions suggest that the water chemistry in the study region is heterogeneous and influenced by complex hydrogeochemical process and complex contaminant sources (Vasanthavigar *et al.*, 2012).

The groundwater pH is generally low with values lying in the range 4.77 – 8.10 with the mean and median values of 6.51 and 6.41, respectively during the dry season. In the rainy season, the pH ranged between 4.90 and 8.28 with the mean and median values of 6.40 and 6.40 respectively. The groundwater is slightly acidic with majority of the samples (over 80%) lying within the range 4.5 to 6.9 which falls within natural water pH values of between 4.5 and 9.0 (Langmuir, 1997). Thus in terms of pH, the groundwater samples are portable. The electrical conductivity (EC) values are in the range 210.85 – 7711.0 $\mu$S cm$^{-1}$ with mean and median values of 1081 $\mu$S cm$^{-1}$ and 853.3 $\mu$S cm$^{-1}$ respectively during the dry season. In the rainy season, the EC values range between 49.16 and 4311.0 $\mu$S cm$^{-1}$ with mean and median values of 837.0 and 728.6 $\mu$S cm$^{-1}$ respectively. This indicates that there are more dissolved ions in solution.

During the rainy season two boreholes at Topiase and Brahabekume had Total Dissolved Solids (TDS) values of 1251.0 mg/L and 2430.0 mg/L respectively, which are above 1000 mg/L. Most of the groundwater samples (96%) have TDS values less than 1000 mg/L recommended for domestic water, which are classified as fresh water (WHO, 2008). The TDS values range between 24.635 mg/L and 2430.0 mg/L with a mean of 457.9 mg/L and median value of 393.8 mg/L. In the dry season, the TDS values ranged between 101.7 mg/L and 3062.0 mg/L with a mean of 513.8 mg/L and a median value of 401.3 mg/L. Four boreholes at Gyangyanadze, Aduafokwaa, Topiase and Brahabekume had TDS values of 1247.0 mg/L, 1084.0 mg/L, 1331.0 mg/L and 3062.0 mg/L respectively, which are classified as high salinity waters. The water samples from these boreholes are therefore not portable. Gyangyanadze is near the coast, Aduafokwa is also not far from the coast but Brahabekume is located in the middle portion of the Ayensu basin in a low-lying flood prone area. Topiase however is located on a hill far inland.

During the rainy season, in most of water samples (>72%) $Na^+$ shows a clear dominance but in few cases either $Ca^{2+}$ or $Mg^{2+}$ appear to be the dominant cation. $Na^+$ ranges from 27.0 mg/L to 656.0 mg/L, with a mean of 106.7 mg/L. In the dry season also, $Na^+$ showed a clear dominance (63.3%). The $Na^+$ concentration ranged from 8.50 mg/L to 510.5 mg/L with a mean of 83.36 mg/L. The dominant anion in the water samples in both the dry and rainy seasons is $Cl^-$ followed by $SO_4^{2-}$, $HCO_3^-$ and then $NO_3^-$.

Chloride ion ($Cl^-$) varies from 46.29 mg/L to 1524.0 mg/L with a mean of 195.1 mg/L during the dry season. During this period, 13.3% of the water samples (8 boreholes) exceeded the permissible levels of 250mg/L for $Cl^-$ ion (WHO, 2008). For the rainy season, the $Cl^-$ ion concentration varied from 85.30 mg/L to 1680.1 mg/L and a mean value of 225.4 mg/L. In this season, 16.7% (10 boreholes) had their $Cl^-$ ion concentration exceeding the WHO permissible level. High chloride concentration increases the electrical conductivity of water and thus increases its corrosivity. In metal pipes, chloride reacts with metal ions to form soluble salts (WHO, 1978), thus increasing levels of metals in drinking-water. In lead pipes, a protective oxide layer is built up, but chloride enhances galvanic corrosion (Gregory, 1990). It can also increase the rate of pitting corrosion of metal pipes (DNHW, 1978).

Approximately 27% of the groundwater samples have their $NO_3^-$ concentrations exceeding the WHO maximum acceptable limit of 50 mg/L in the rainy season. This may cause health problems for infants using such waters as source of drinking water. During the dry season, all the $NO_3^-$ values were below the WHO acceptable limit of 50 mg/L. Borehole waters with $NO^{3-}$ concentration above 50 mg/L are not suitable for use as drinking water for infants.

Table 23: Statistical summary of the parameters determined in the 60 water samples in the dry season.

| | Minimum | Maximum | Mean | Median | STD | WHO Guideline limit |
|---|---|---|---|---|---|---|
| Temp | 21.1 | 30.4 | 25.91 | 26.25 | 2.153 | |
| pH | 4.77 | 8.1 | 6.508 | 6.41 | 0.803 | 6.5 – 8.5 |
| EC | 210.85 | 7711 | 1081 | 853.3 | 853.3 | |
| TDS | 101.7 | 3062 | 513.8 | 401.3 | 434.4 | |
| Alk. | 1.2 | 33.4 | 12.25 | 10.93 | 7.087 | |
| Ca | 7.2 | 625 | 50.86 | 38.35 | 78.04 | |
| Mg | 1.46 | 122 | 27.05 | 23.18 | 19.62 | |
| Na | 8.5 | 510.5 | 83.36 | 63.5 | 80.76 | 200.0 |
| K | 1.5 | 73.0 | 10.25 | 7.6 | 11.72 | |
| $HCO_3^-$ | 1.464 | 40.75 | 14.95 | 13.33 | 8.647 | |
| $Cl^-$ | 46.29 | 1524.0 | 195.1 | 161.4 | 200.5 | 250.0 |
| $SO_4^{2-}$ | 43.46 | 406.0 | 191.5 | 94.6 | 165.6 | 250.0 |
| $NO_3^-$ | 0.006 | 18.0 | 1.543 | 0.145 | 3.82 | 50.0 |
| $PO_4^{3-}$ | 0.00 | 17.75 | 1.10 | 0.16 | 2.77 | |
| Zn | 0.025 | 0.465 | 0.150 | 0.141 | 0.086 | 3.000 |
| Cu | <0.003 | 1.112 | 0.579 | 0.872 | 0.484 | 2.000 |
| Fe | <0.006 | 1.080 | 0.659 | 0.642 | 0.432 | 0.300 |
| Cr | <0.006 | 1.01 | 0.179 | 0.148 | 0.194 | 0.050 |
| Cd | <0.002 | 0.082 | 0.046 | 0.038 | 0.031 | 0.003 |
| Mn | <0.002 | 0.561 | 0.096 | 0.043 | 0.138 | 0.500 |
| Al | <0.030 | 3.58 | 1.740 | 2.044 | 1.214 | 0.200 |
| Salinity | 0.096 | 3.319 | 0.533 | 0.413 | 0.471 | |
| $SiO_2$ | 12.8 | 102.02 | 64.077 | 64.90 | 16.86 | |

Temp. in °C, pH in pH-units, EC in µS $cm^{-1}$, TDS to $SiO_2$ in $mgl^{-1}$

Table 24: Statistical summary of the parameters determined in the 60 water sample in the rainy season.

| | Minimum | Maximum | Mean | Median | STD | WHO guideline limit |
|---|---|---|---|---|---|---|
| Temp. | 21.6 | 31.7 | 27.38 | 27.4 | 1.425 | |
| pH | 4.9 | 8.28 | 6.395 | 6.395 | 0.869 | 6.5 – 8.5 |
| EC | 49.16 | 4311.0 | 837.0 | 728.6 | 616.6 | |
| TDS | 24.635 | 2430.0 | 457.9 | 393.8 | 335.7 | |
| Alk. | 6.57 | 80.0 | 28.6 | 25.5 | 13.0 | |
| Ca | 26.0 | 146.96 | 52.54 | 42.5 | 26.38 | |
| Mg | 6.05 | 192.9 | 35.22 | 25.9 | 30.13 | |
| Na | 27.0 | 656.0 | 106.7 | 85.08 | 105.3 | 200.0 |
| K | 1.5 | 53.0 | 8.528 | 6.95 | 7.71 | |
| $HCO_3^-$ | 16.495 | 97.6 | 35.17 | 30.93 | 15.59 | |
| $Cl^-$ | 85.301 | 1680.1 | 225.4 | 167.9 | 242.9 | 250.0 |
| $SO_4^{2-}$ | 33.21 | 406.0 | 94.28 | 77.45 | 61.17 | 250.0 |
| $NO_3^-$ | 0.00 | 155.28 | 38.77 | 23.98 | 40.72 | 50.0 |
| $PO_4^{3-}$ | 0.00 | 17.748 | 1.202 | 0.532 | 2.852 | |
| Zn | 0.002 | 0.388 | 0.098 | 0.0716 | 0.088 | 3.000 |
| Cu | <0.003 | 0.353 | 0.0488 | 0.0125 | 0.099 | 2.000 |
| Fe | <0.006 | 4.245 | 0.31 | 0.00 | 0.70 | 0.300 |
| Cr | <0.001 | 0.01 | 0.006 | 0.0065 | 0.003 | 0.050 |
| Cd | <0.002 | 0.082 | 0.067 | 0.076 | 0.023 | 0.003 |
| Mn | <0.002 | 0.391 | 0.071 | 0.0345 | 0.097 | 0.500 |
| Al | <0.030 | 0.438 | 0.261 | 0.276 | 0.093 | 0.200 |
| Salinity | 0.11 | 3.035 | 0.523 | 0.462 | 0.411 | |

## Saturation Indices

The saturation state of the groundwater was assessed with respect to the major carbonate minerals in order to investigate the thermodynamic controls on the composition of the groundwater and the approximate degree to which the groundwater has equilibrated with the various carbonate phases. Table 25 shows the summary statistics of saturation indices of some of the common mineral phases. The saturation indices indicate that the groundwater in the study area is undersaturated with respect to gypsum, anhydrite and halite but not albite. Approximately 86.7% of the water samples are supersaturated with respect to albite and 13.3% are undersaturated in certain places. The groundwaters are supersaturated with respect to quartz but undersaturated with respect to amorphous silica suggesting that amorphous silica possibly controls the silica concentration in the groundwater (Kortatsi, 2007).

A plot of computed saturation indices for calcite and dolomite (the commonest carbonate phases) for the groundwater samples is shown in Fig. 31. In the diagram, calcite saturation is indicated on the ordinate and dolomite on the abscissa.

A central band, of 0.4 units wide along each axis, represents essential equilibrium with respect to either mineral to account for the possible errors that may occur in the measurement of pH, $Mg^{2+}$ and $Ca^{2+}$.

Table 25: Statistical summary of saturation indices for carbonate, iron bearing minerals, gypsum, albite, anhydrite, amorphous silicate and quartz.

| Parameter | Min. | Max. | Mean | Median | Std. |
|---|---|---|---|---|---|
| pH | 4.77 | 8.10 | 6.32 | 6.13 | 0.745 |
| Si_ Albite | -2.4 | 2.53 | 1.03 | 1.44 | 1.34 |
| Si_ Anhydrite | -3.11 | -1.36 | -2.02 | -2.05 | 0.35 |
| Si_ Calcite | -263.08 | -0.29 | -129.76 | -127.82 | 129.303 |
| Si_ Dolomite | -525.47 | -0.39 | -259.33 | -255.28 | 258.57 |
| Si_ $Fe(OH)_3$(a) | -0.97 | 0.17 | -0.32 | -0.28 | 0.24 |
| Si_ Goethite | 4.7 | 8.72 | 7.36 | 7.72 | 1.12 |
| Si_ Gypsum | -2.9 | -1.13 | -1.8 | -1.83 | 0.35 |
| Si_ Halite | -7.45 | -5.32 | -6.48 | -6.42 | 0.45 |
| Si_ Hematite | 11.4 | 19.47 | 16.75 | 17.46 | 2.23 |
| Si_ $SiO_2$(a) | -0.97 | -0.06 | -0.30 | -0.28 | 0.17 |
| Si_ Quartz | 0.27 | 1.19 | 0.93 | 0.95 | 0.17 |
| $H_4SiO_4/Na^+$ | 0.02 | 1.37 | 0.41 | 0.33 | 0.28 |
| $H_4SiO_4/HCO_3^-$ | 0.00 | 364 | 14.8 | 0.96 | 65.0 |
| $Fe^{2+}/SO_4^{2-}$(Molar ratio) | 0.00 | 0.197 | 0.013 | 0.006 | 0.030 |

The four quadrants of the plotting field, I- IV, outside the equilibrium area, represent different kinds of equilibrium conditions with respect to calcite and dolomite. Quadrant I represents super-saturation with respect to both carbonates. This condition represents water brought to equilibrium with respect to these carbonates and subsequently transported into a different environment where a higher pH or an apparent condition caused by the failure of the measured pH to accurately represent the actual equilibrium pH of the water in the aquifer (Langmuir, 1971; Kortatsi, 2007). Quadrant II, represent super-saturation with respect to calcite but undersaturation with respect to dolomite. Water undergoing incongruent dissolution of dolomite or precipitation of calcite would plot in the quadrant. Quadrant III, represent undersaturation with respect to both calcite and dolomite. A sample plotting in this quadrant represents water that has come from an environment where carbonates are impoverished. Water that has not reached equilibrium with the carbonates due to the short residence time would plot in this quadrant (Langmuir, 1971; Kortatsi 2007). Quadrant IV represents super-saturation with respect to dolomite and undersaturation with respect to calcite.

All the groundwater samples plotted in quadrant III, indicating that the groundwater is undersaturated with respect to the major carbonate species. Thus, either the groundwater originates from an environment where calcite and dolomite are impoverished or the residence time is short and has inadequate time for the mineral phases to react to equilibrium.

The stability diagram of albite and its possible weathering products gibbsite, kaolinite and Na- montmorillonite (Tardy, 1971) for the groundwaters in the Ayensu Basin is shown in Fig. 32.

Thermodynamic plotting of $[Na^+]/[H^+]$, for groundwater from study area are plotted on the stability diagram as a function of $[H_2SiO_4]$. Most of the samples cluster in the Na- montmorillonite stability field and a few plot in the kaolinite stability field, indicating Na–Montmorillonite is the end product of the silicate weathering. This is consistent with the relatively low rainfall and poorly drained soils in the lower Ayensu basin.

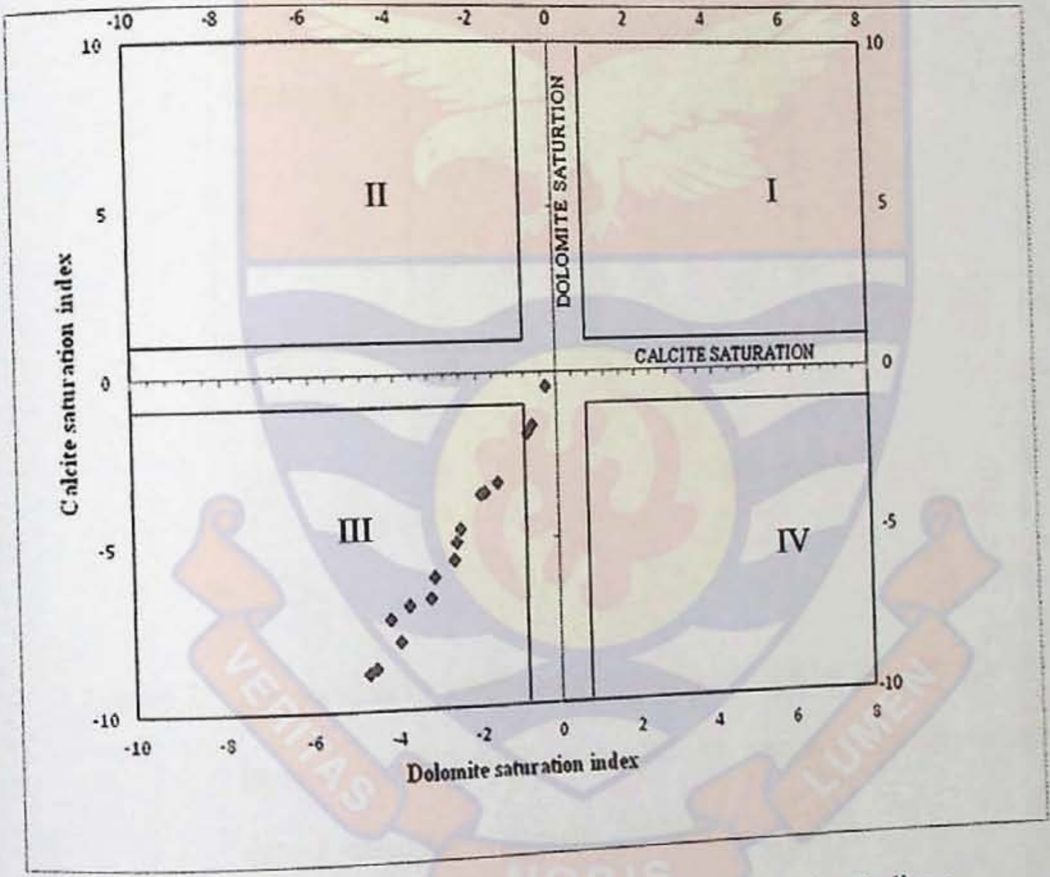

Figure 31: Plot of calcite versus dolomite saturation indices

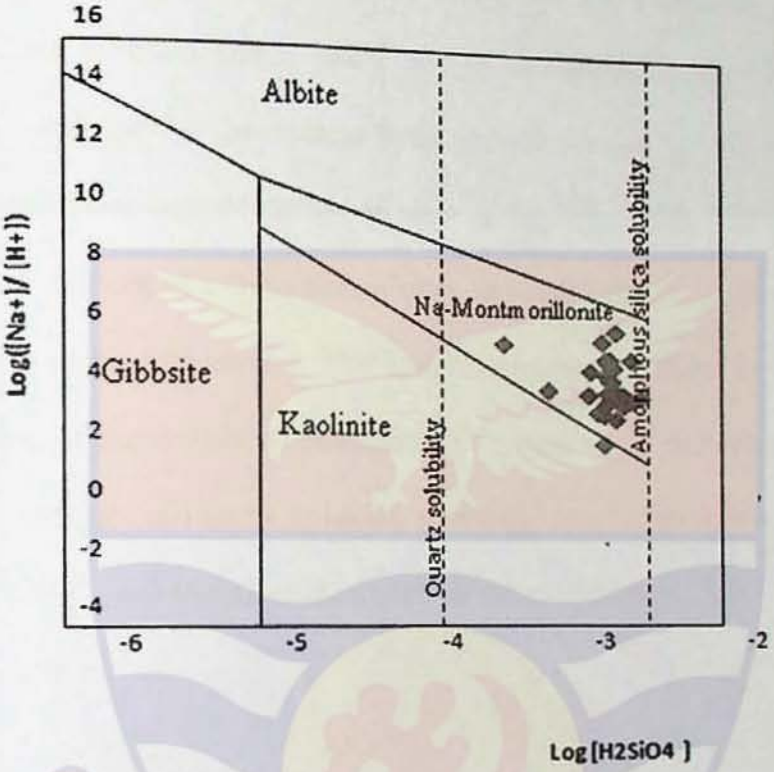

Figure 32: The stability of albite and its possible weathering products gibbsite, kaolinite and Na-montmorillonite with respect to the grounwaters in the Ayensu Basin (Kortatsi 2007).

**Silicate weathering**

The groundwater composition is influenced by the reaction between the mineralogy of the rocks underlying the Ayensu Basin and the groundwater. The degree to which the mineral phases react with the groundwater depends on the availability of protons ($H^+$), the contact time and the surface area per unit volume of water (Hem, 1985). The forest vegetation and the humid climatic conditions of the Ayensu Basin provide avenues for the decay of leaves and other organic matter as well as root respiration that produce substantial amount of $CO_2$ in the soil zone and hence the $H^+$ availability for circulation in the groundwater. This process commences with the incongruent dissolution of aluminosilicate minerals by $CO_2$ enriched groundwaters, which convert feldspars and micas to kaolin, with a corresponding increase in $Na^+$, $Ca^{2+}$, $K^+$, $Mg^{2+}$, and $H_2SiO_4$ relative to $H^+$ (Stumm & Morgan, 1970).

For example:

$$NaAlSi_3O_8 + H^+ + 4.5\ H_2O <=> 0.5\ Al_2Si_2O_5(OH)_4 + Na^+ + 2H_4SiO_4$$

(albite) (kaolinite)

Following further weathering and the increased availability of silica and cations, the kaolinite can then be converted into montmorillonite as follows:

$$3.5Al_2Si_2O_5(OH)_4 + Na^+ + 4H_4SiO_4 <=> NaAl_7Si_{11}O_{30}(OH)_6 + H^+ + 11.5H_2O$$

(kaolinite) (Na-montmorillonite)

$$1.17Al_2Si_2O_5(OH)_4 + 0.167Ca^{2+} + 1.33H_4SiO_4 <=> CaO_{0.167}Al_{2.33}Si_{3.67}O_{10}(OH)_2 + 0.33H^+ + 3.83H_2O$$

(Kaolinite) (Ca-montmorillonite)

The implication is that the sediment-water system is closed, and, therefore, there is no loss of ions from the system. However, in natural systems, when feldspar-rich igneous rocks are infiltrated by aggressive recharge waters rich in $CO_2$, they are leached of cations and silica. While the initial response is to form gibbsite, the amount of silica cations released is normally more than sufficient to convert the gibbsite to kaolinite (Stumm & Morgan, 1970). As the process proceeds, the cation and silica concentrations steadily increase to a point where the kaolinite starts converting into Montmorillonite (Fig. 32).

## Correlation Coefficient

Correlation coefficient is commonly used to establish the relation between independent and dependent variables (Nair *et al.*, 2005). Strong ($r = 0.8$ to 1.0), moderate ($r = 0.6$ to 0.8) and low ($r = 0.5$ to 0.6) correlation between selected variables was found out.

There is a good correlation between the conductivity (EC) and, $Na^+$, $Cl^-$, $Mg^{2+}$, $Ca^{2+}$, $SO_4^{2-}$ and TDS during the two seasons of this study. Identically, a good correlation exists between TDS and $Na^+$, $Cl^-$, $Ca^{2+}$, $Mg^{2+}$ and $SO_4^{2-}$. This high positive correlation implies that TDS or salinity is derived from these ions. For most of the ions however, there is no significant correlation between them, suggesting that aquifer chemistry is mainly controlled by TDS, EC, $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$ and $Cl^-$. $HCO_3$- shows no significant correlation with any variable. $K^+$ shows no significant correlation with any of the parameters except in the rainy season when it moderately correlated with $SO_4^{2-}$ and $Cl^-$ ($r = 0.7$).

Good, medium and low correlation between chemical parameters indicates that electrical conductivity and total dissolved solids is the most appropriate variable in explaining the variation in hardness, sodium, magnesium, sulphate, chloride and bicarbonate (Pattanaik., 2007). The major exchangeable ions, EC and Na (0.6 and 0.8), Na and Cl (0.8), TDS and Na (0.7 and 0.8), Mg and Cl (0.8), Na and $SO_4^{2-}$ (0.8) were found to be correlated positively indicating the origin of major cations to be dissolution/precipitation processes (Khatiwada *et al*., 2002). Cl and Na possess a very good positive correlation (0.8 and 0.9 in the dry and rainy seasons) between each other indicating that are coming from the same source. The dissolution of halite in water release equal concentrations of Na and Cl into the solution (Belkhiri *et al*., 2010).

The correlation matrix of 13 parameters, for the 60 water samples in the study area is indicated in Tables 26 and 27.

*Table 26:* Pearson correlation matrix for the dry season

| | pH | EC | TDS | ALK | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}$ | $K^{+}$ | $Cl^{-}$ | $SO_4^{2-}$ | $HCO_3^{-}$ | $NO_3^{-}$ | $PO_4^{2-}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 1 | | | | | | | | | | | | |
| EC | 0.1 | 1 | | | | | | | | | | | |
| TDS | 0.2 | 1 | 1 | | | | | | | | | | |
| ALK | 0.4 | 0.3 | 0.3 | 1 | | | | | | | | | |
| $Ca^{2+}$ | 0.1 | 0.9 | 0.8 | 0.2 | 1 | | | | | | | | |
| $Mg^{2+}$ | 0.0 | 0.8 | 0.8 | 0.3 | 0.6 | 1 | | | | | | | |
| $Na^{+}$ | 0.2 | 0.6 | 0.7 | 0.1 | 0.4 | 0.7 | 1 | | | | | | |
| $K^{+}$ | 0.0 | 0.1 | 0.2 | 0.1 | 0.0 | 0.2 | 0.2 | 1 | | | | | |
| $Cl^{-}$ | 0.1 | 0.9 | 0.9 | 0.2 | 0.9 | 0.8 | 0.8 | 0.1 | 1 | | | | |
| $SO_4^{2-}$ | 0.1 | 0.7 | 0.7 | 0.1 | 0.5 | 0.7 | 0.8 | 0.1 | 0.7 | 1 | | | |
| HCO3- | 0.4 | 0.3 | 0.3 | 1.0 | 0.2 | 0.3 | 0.1 | 0.1 | 0.2 | 0.1 | 1 | | |
| NO3- | 0.0 | -0.1 | -0.1 | -0.1 | -0.1 | -0.3 | -0.1 | -0.1 | -0.1 | -0.3 | -0.1 | 1 | |
| PO43- | -0.2 | -0.1 | -0.1 | 0.0 | -0.1 | 0.1 | -0.1 | -0.1 | -0.1 | 0.0 | 0.0 | -0.1 | 1 |

Table 27: Pearson correlation matrix for the rainy season

| | pH | EC | TDS | ALK | $Ca^{2+}$ | $Mg^{2+}$ | $Na^{+}$ | $K^{+}$ | $Cl^{-}$ | $SO_4^{2-}$ | $HCO_3^{-}$ | $NO_3^{-}$ | $PO_4^{3-}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 1 | | | | | | | | | | | | |
| EC | 0.072 | 1 | | | | | | | | | | | |
| TDS | 0.09 | 1 | 1 | | | | | | | | | | |
| ALK | 0.32 | 0.2 | 0.2 | 1 | | | | | | | | | |
| $Ca^{2+}$ | 0.05 | 0.5 | 0.5 | 0.3 | 1 | | | | | | | | |
| $Mg^{2+}$ | 0.01 | 0.7 | 0.8 | 0.1 | 0.4 | 1 | | | | | | | |
| $Na^{+}$ | 0.07 | 0.8 | 0.8 | 0.1 | 0.5 | 0.6 | 1 | | | | | | |
| $K^{+}$ | 0.02 | 0.6 | 0.6 | 0.1 | 0.1 | 0.6 | 0.6 | 1 | | | | | |
| $Cl^{-}$ | 0.08 | 0.9 | 0.9 | 0.1 | 0.5 | 0.8 | 0.9 | 0.7 | 1 | | | | |
| $SO_4^{2-}$ | 0.00 | 0.8 | 0.8 | 0.2 | 0.4 | 0.7 | 0.9 | 0.7 | 0.8 | 1 | | | |
| $HCO_3^{-}$ | 0.33 | 0.2 | 0.2 | 1.0 | 0.3 | 0.1 | 0.1 | 0.1 | 0.1 | 0.18 | 1 | | |
| $NO_3^{-}$ | 0.06 | 0.1 | 0.1 | 0.3 | 0.3 | 0.1 | 0.0 | 0.1 | 0.0 | 0.03 | 0.24 | 1 | |
| $PO_4^{3-}$ | -0.20 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.1 | 0.1 | 0.0 | 0.05 | 1 |

**Hydrochemical facies**

Facies are recognizable parts of different characters belonging to any genetically related system. Hydrochemical facies are distinct zones that possess cation and anion concentration categories. To define composition class, Back and co-workers (1965), suggested subdivisions of the tri-linear diagram. The interpretation of distinct facies from the 0 to 10% and 90 to 100% domains on the diamond shaped cation to anion graph is more helpful than using equal 25% increments. It clearly explains the variations or domination of cation and anion concentrations during the dry season and rainy season (Sadashivaiah *et al*, 2008).

In the cation plot field for the dry season, most of the samples plot mainly towards the Na+K corner indicating sodium type or potassium type waters whilst some plotted towards the middle indicating no dominant anion type. A few plot in the calcium water type. In the anion plot field the samples mostly plotted towards the $Cl^-$ corner indicating chloride type water, but some of the samples plotted towards the $SO_4^{2-}$ type water. Most of the boreholes and hand dug wells and a few surface waters cluster towards the Na-Cl section during the dry season. A few surface and hand dug well waters and some boreholes show Ca-Mg-Cl water type and also Ca- Mg-$SO_4$ water type as shown in Figure 33.

During the rainy season as shown in Figure 34, in the cation field, some of the water samples plot towards Na+K corner indicating sodium or potassium water types with others plotting in the middle indicating no dominant cation. A few of the water samples plot in the magnesium water type. In the anion plot field most of the samples plotted towards the $Cl^-$ corner indicating chloride type water and the other water samples plotted in the no dominant anion field. All the rainwater samples plotted in the $CO_3^{2-}+HCO_3^-$ type waters. The surface waters and the hand dug wells plot mainly in the mixed water section where there is neither dominant cation or anion. Most of the boreholes cluster towards the Na-Cl section, however a few of the boreholes and surface waters show Mg-Ca-Cl and Mg- Ca-$SO_4$ water types as shown in Figure 34.

The ionic dominance pattern for the water samples in both the dry and rainy seasons were $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $Cl^- > SO4^{2-} > HCO_3^- > NO_3^-$. There is no significant change in the hydro-chemical facies noticed during the study period (dry and rainy seasons), which indicates that most of the major ions are natural in origin. The reason is groundwater passing through igneous rocks dissolves only small quantities of mineral matters because of the relative insolubility of the rock composition ( Sadashivaiah *et al*, 2008).

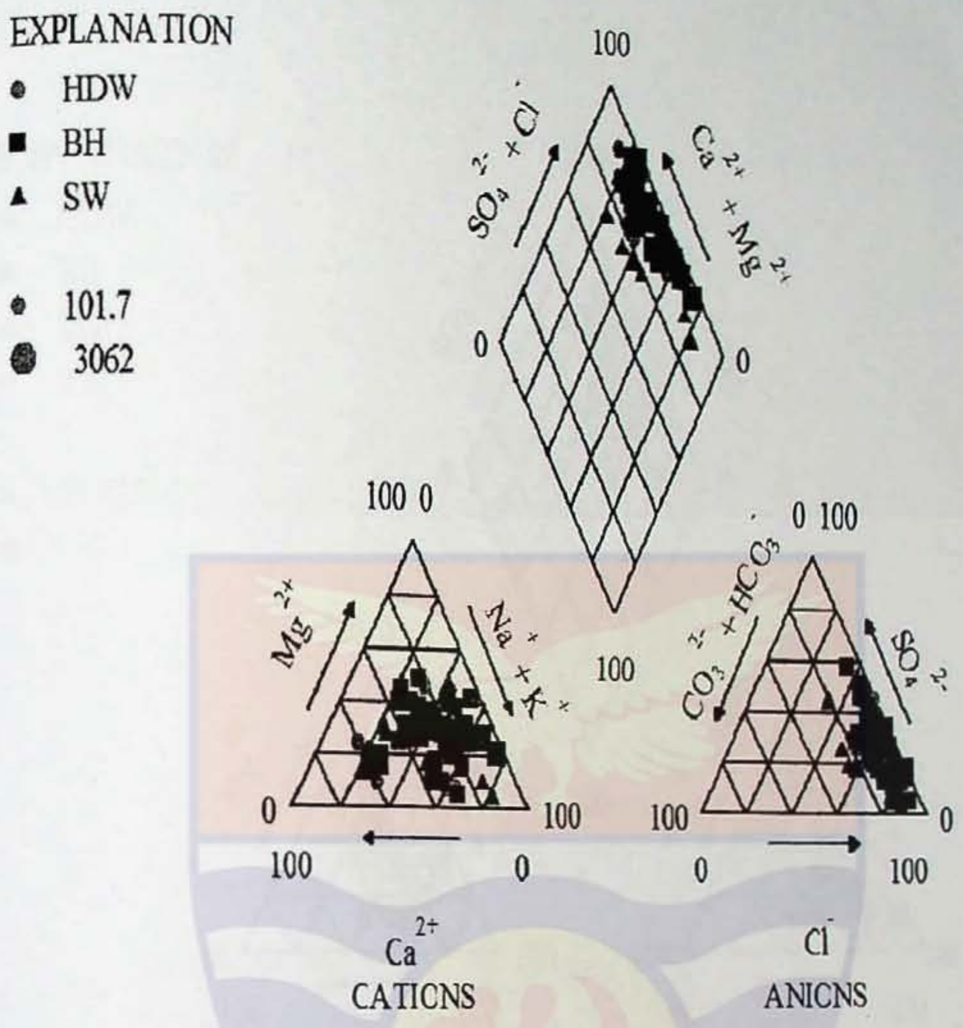

Figure 33: Piper diagram for the dry season

HDW= HAND DUG WELL; BH= BOREHOLE;

SW= SURFACE WATER; RW= RRAINWATER

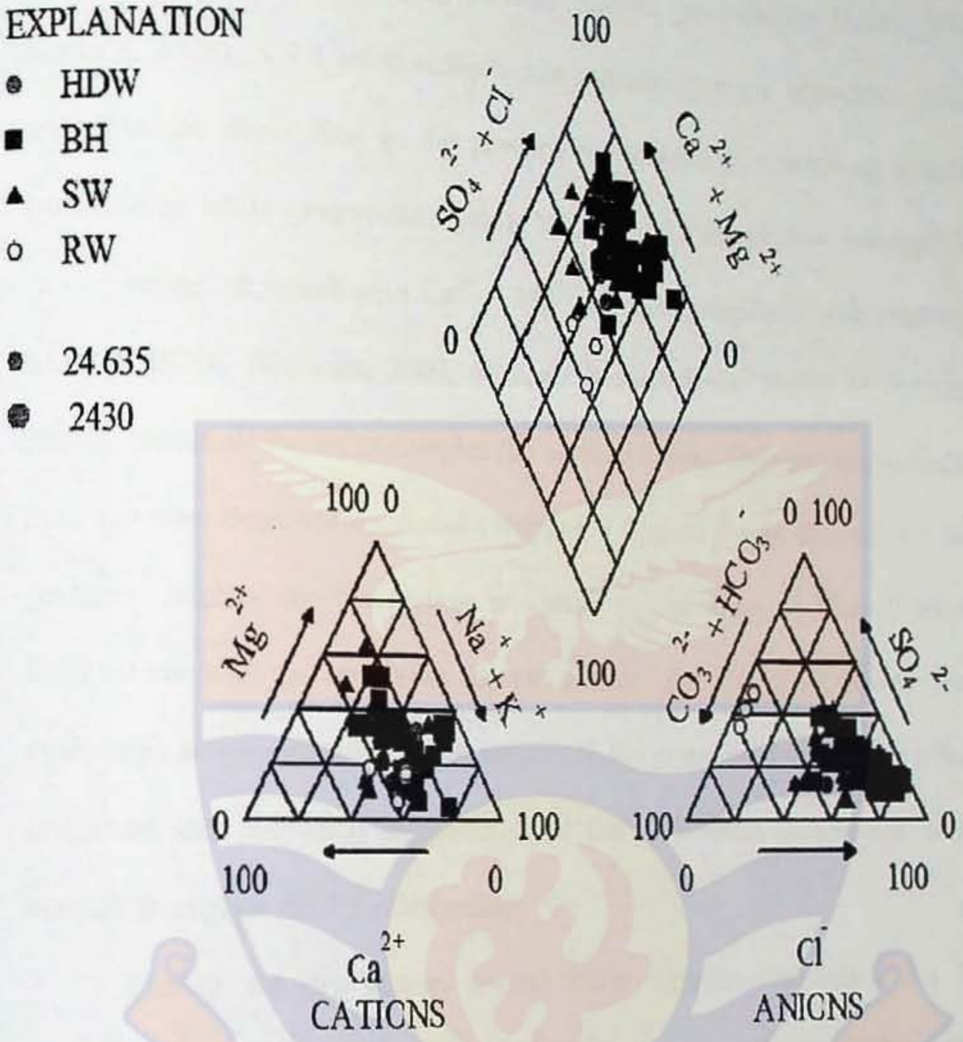

Figure 34: Piper diagrams for the rainy season

HDW= HAND DUG WELL; BH= BOREHOLE;

SW= SURFACE WATER; RW= RRAINWATER

**Sources of Major Ions**

Relationships between major cations and anions have been employed to deduce the probable sources of these ions in groundwater (Jalali, 2007; Kortatsi, 2006). A 1:1 relationship would indicate gypsum, anhydrite, calcite and dolomite dissolution as the predominant processes controlling solution composition while groundwater falling below the 1:1 dissolution line signifies ion exchange, in which case $Ca^{2+} + Mg^{2+}$ are being depleted with respect to $SO_4^{2-} + HCO_3^-$ (Kortatsi, 2007; McLean & Jankowski, 2000). In the rainy season almost all the water samples fall on the 1:1 line. Gypsum and anhydrite have not been detected in the rocks within the Ayensu Basin, thus the 1:1 ratio probably implies the dissolution of calcite or dolomite or both (Kortatsi, 2007). However, the saturation indexes indicate that the groundwater in the study area is undersaturated with respect to the common carbonates (calcite. aragonite and dolomite) suggesting that the carbonates dissolution is not enough to explain the 1:1 relationship.

During the dry season several water samples fall below 1:1 line signifying ion exchange, in which case $Ca^{2+} + Mg^{2+}$ are being depleted with respect to $SO_4^{2-} + HCO_3^-$ (McLean and Jankowski, 2000). The $Mg^{2+}/Mg^{2+} + Ca^{2+}$ equivalent ratio for over 50% of the water samples is greater than 0.5 and the $HCO_3^-/SiO_2$ for almost all the water samples were very low, varying between 0.02 and 1.3 suggesting silicate weathering is likely (Hounslow, 1995; Kortatsi, 2007). Thus, silicate weathering may have contributed significantly to the concentration of the $Ca^{2+}$ and $Mg^{2+}$. The groundwater sample plots with the relatively high TDS, lie largely below the 1:1 line. This indicates that the cations $Ca^{2+}$ and $Mg^{2+}$ react with other anions and produce carbonate minerals. As a result, the total concentration of $[Ca^{2+} + Mg^{2+}]$ reduces (Deng *et al*, 2007). Thus Ca and Mg are being lost through cation exchange or precipitation as insoluble Ca and Mg salts. This can seen in figures 35 and 36.

Na/Cl molar ratios have been used to determine whether halite dissolution or silicate weathering is contributing to the hydrochemistry of the groundwater. The Na–Cl relationships have often been used to identify the mechanisms for acquiring salinity and saline intrusions (Jalali, 2007; Dixon & Chiswell, 1992). For the rainy season, as shown in Fig. 38, approximately 81% of the water samples have $Na^+/(Na^+ + Cl^-)$ ratio within the range 0.5 ± 0.1 or plot along or close to 1:1 line in the graph of $[Na^+]$ versus $[Cl^-]$. This suggests that either sea aerosols or halite dissolution is responsible for $Na^+$ in the groundwater. Since halite is not known to be associated with the rocks in the Ayensu Basin, it implies that sea aerosols is partially the likely source of sodium in the groundwater (Kortatsi, 2007). A few (5%) of the water samples fall above the 1:1 line (i.e. the milliequivalent concentration of most $Na^+$ is greater than that of $Cl^-$) which reflects a release of Na from other sources such as silicate weathering or cation exchange but are not major processes influencing chemical evolution in the river basin. This is mainly ascribed to $Na^+$ released from feldspar through hydrolysation and acid attack during the groundwater flow and ion- exchange of $Ca^{2+}$ in water for $Na^+$ in soil (Deng *et al*, 2007). During the same season, i.e. the rainy season, 14% of the samples plot below and away from the 1:1 line of the $[Na^+]$ versus $[Cl^-]$ graph, indicating that reverse ion exchange is also occurring in the Basin.

In the dry season (Fig. 37), most of the water samples plot along or close to the 1:1 line in the [$Na^+$] versus [$Cl^-$] graph. This suggests the possible sources of $Na^+$ and $Cl^-$ as direct seawater intrusion, sea aerosol sprays or dissolution of soluble salts in the soil horizons. The rocks that underlain the Basin are granites which are impermeable and so the possibility of direct seawater intrusion is ruled out. Sea aerosol spray could be responsible for the high Na and Cl contents of the groundwaters. The other possibility is the dissolution of soluble salts in the soil horizons. Salts could have been formed as a result of aerosol deposition or ancient seawater flooding in the area. A few water samples fell above the 1:1 line suggesting other sources of $Na^+$ (silicate weathering or cation exchange) and also below and away from the 1:1 line of the [$Na^+$] and [$Cl^-$] graph suggesting that reverse ion-exchange is occurring but is not a major process controlling the chemical evolution of groundwater in the Ayensu Basin.

Rainwater sampled in 2011 at Winneba near the coast, Agona Swedru in the mid portion of the Ayensu Basin and Kwanyako in the northern part had mean $Na^+$ concentrations of 5.10mg/L, 9.10 mg/L and 6.35 mg/L respectively. The mean $Cl^-$ concentrations during the same period were 3.0 mg/L, 6.45 mg/L and 6.57 mg/L respectively for the three stations. The highest values for sodium, 9.30 mg/L and chloride, 35.7 mg/L, occur at the Swedru station. Rainwater is therefore a possible contributor of $Na^+$ and $Cl^-$ to the groundwaters in the Ayensu river Basin.

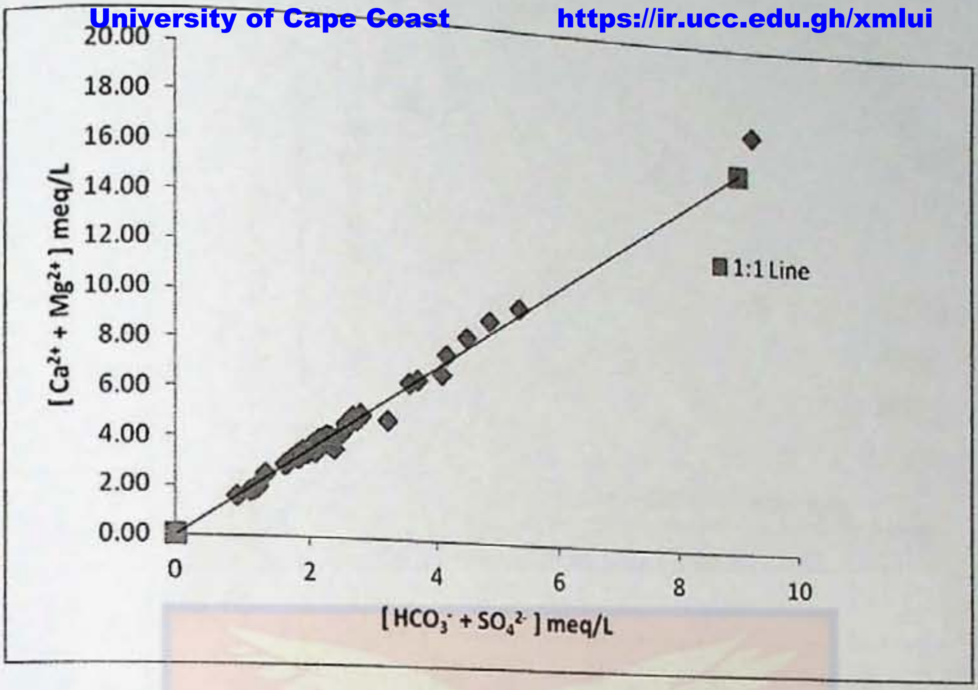

Figure 35: Relationship between [ $Ca^{2+}$ + $Mg^{2+}$ ] versus [ $HCO_3^-$ + $SO_4^{2-}$ ] of the groundwaters of the Ayensu Basin in the rainy season.

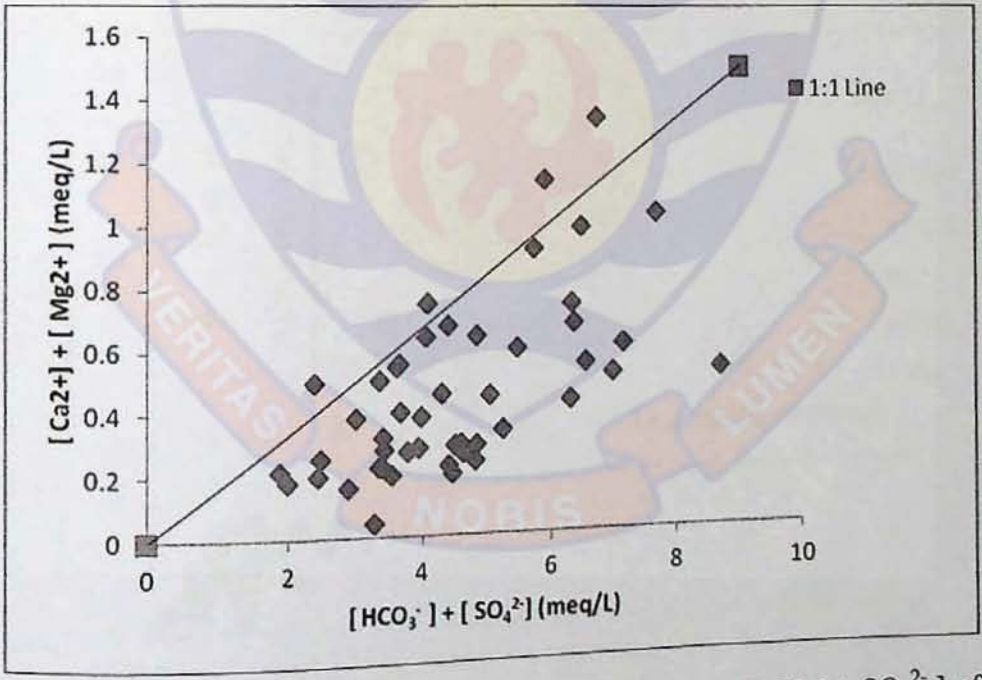

Figure 36: Relationship between [ $Ca^{2+}$ + $Mg^{2+}$ ] versus [ $HCO_3^-$ + $SO_4^{2-}$ ] of the groundwaters of the Ayensu Basin in the dry season.

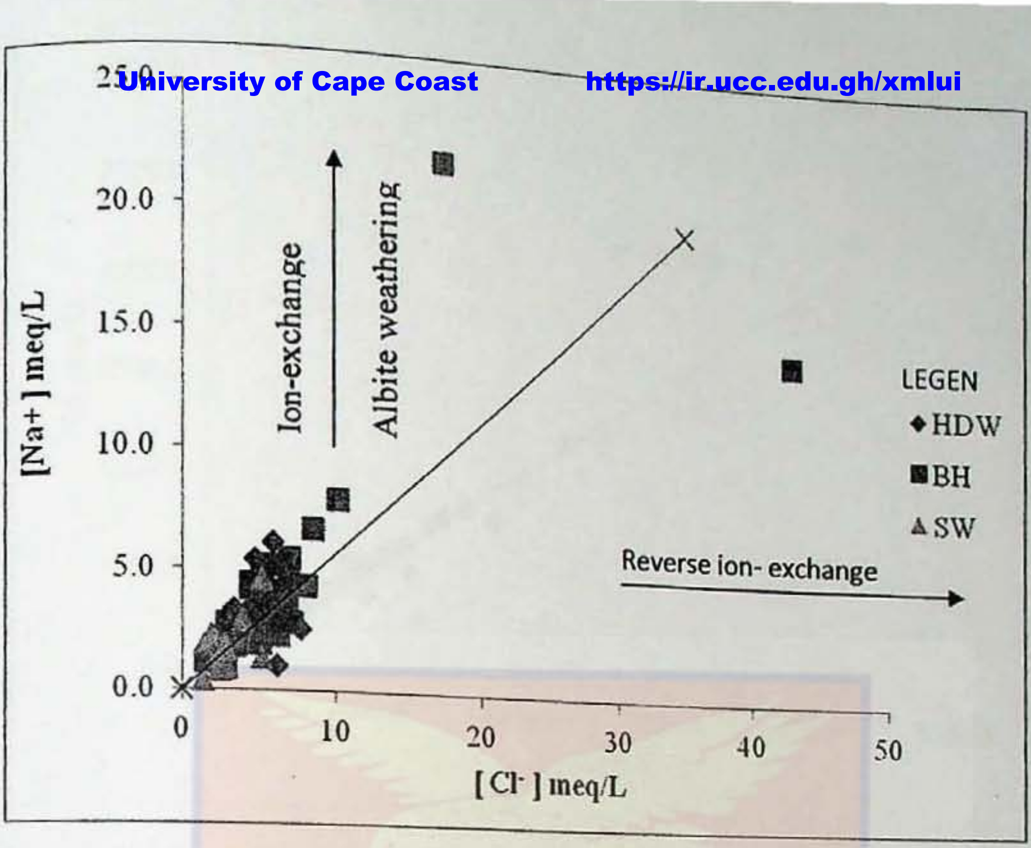

Figure 37: [ $Na^+$] versus [ $Cl^-$] of the water samples in the dry season

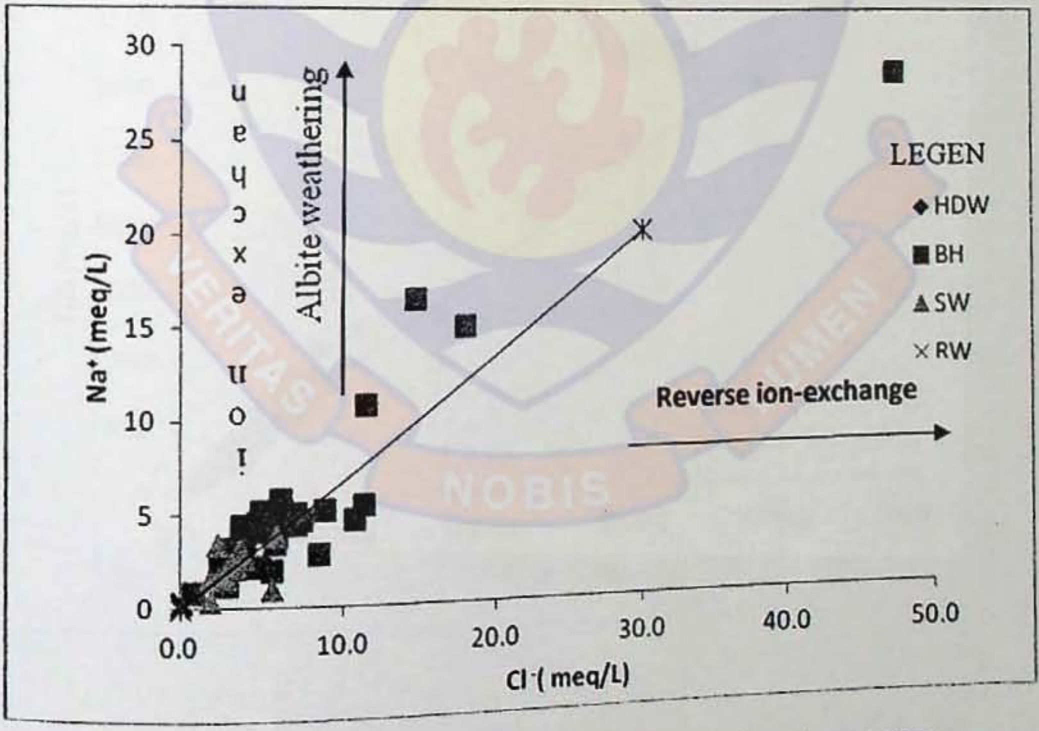

Figure 38: [ $Na^+$] versus [ $Cl^-$] of the water samples in the rainy season

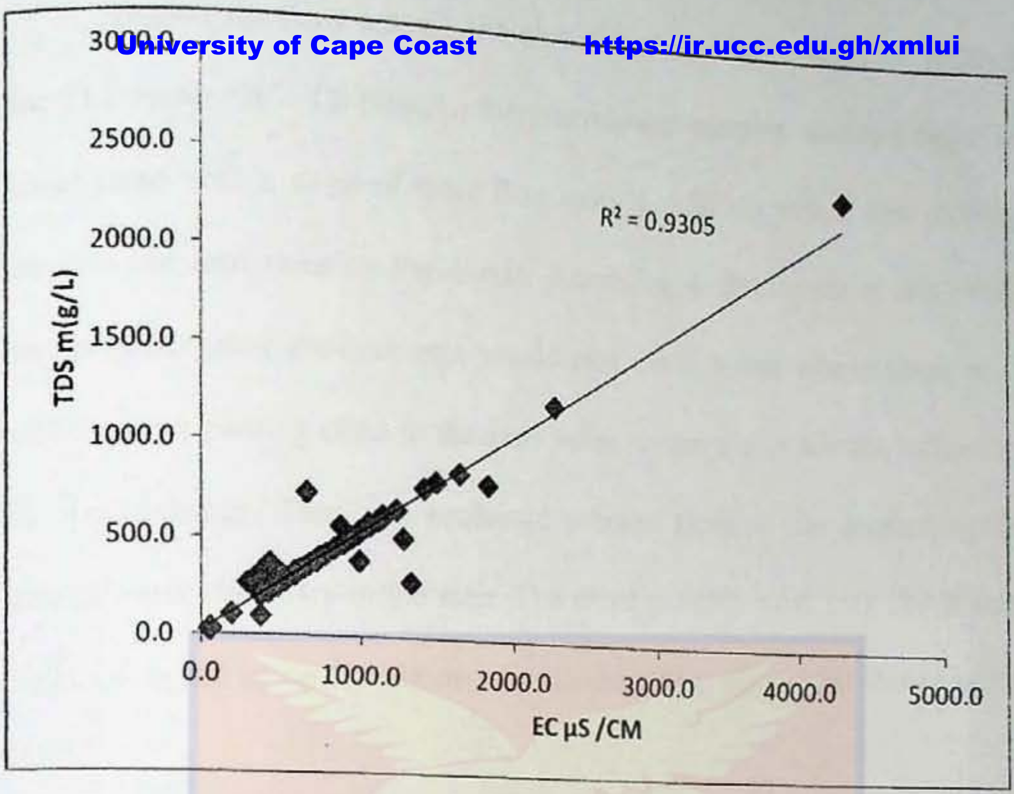

Figure 39: Plot of EC versus TDS for the water samples in the rainy season.

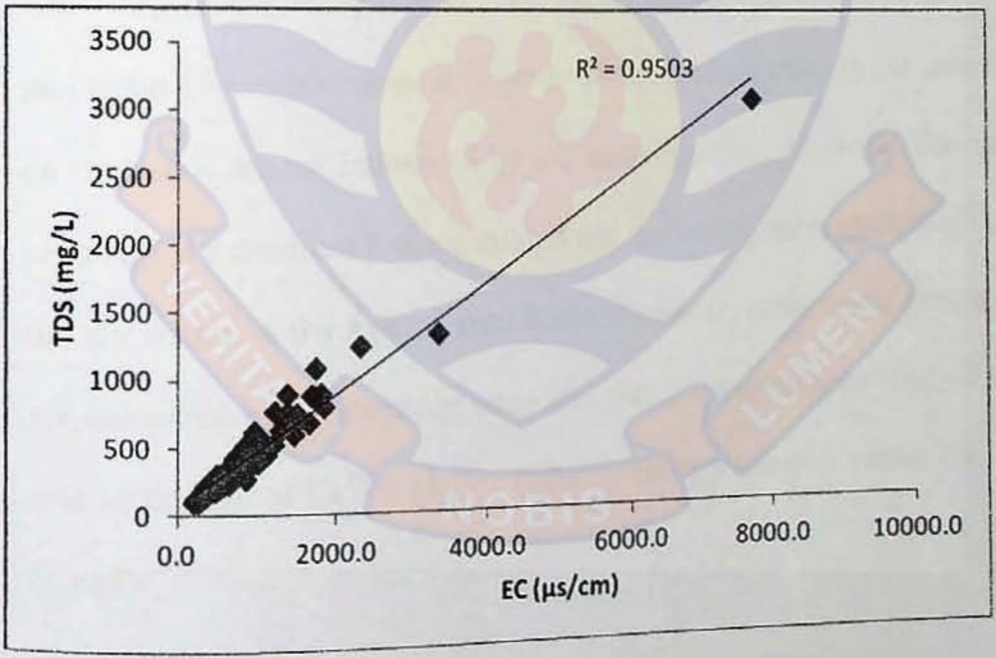

Figure 40: Plot of EC versus TDS for the water samples in the dry season.

During the rainy season, the plot of $Ca^{2+} + Mg^{2+} - (SO_4^{2-} + HCO_3^-)$ (meq/L) versus $Na^+ - Cl^-$ (meq/L) for groundwater samples shows a negative linear trend with a slope of more than unity (- 1.3775) with a few plotting close to the zero value on the x-axis. According to Jankowski *et al* (1998), waters undergoing ion-exchange would plot along a line whose slope is -1 while waters plotting close to the zero value on the x-axis are not influenced by ion-exchange. Thus, ion exchange process alone is not controlling the groundwater chemistry in the area. The other possible processes like silicate weathering and halite dissolution may also be taking place. This shown in Fig. 42.

During the dry season most of the water samples plot along a line whose slope is -1.1 and some plot close to the zero value on the x-axis. According to Jankowski *et al* (1998), waters undergoing ion exchange would plot along a line whose slope is -1 while waters plotting close to the zero value on the x-axis are not influenced by ion exchange. Fig. 41 shows that cation exchange is a dominant process influencing the groundwater chemistry during the dry season in the Ayensu river basin. However, some water samples are not influenced by ion exchange since they plot close to the zero value of the x-axis in the plot of $Ca^{2+} + Mg^{2+} - (SO_4^{2-} + HCO_3^-)$ (meq/L) versus $Na^+ - Cl^-$ (meq/l).

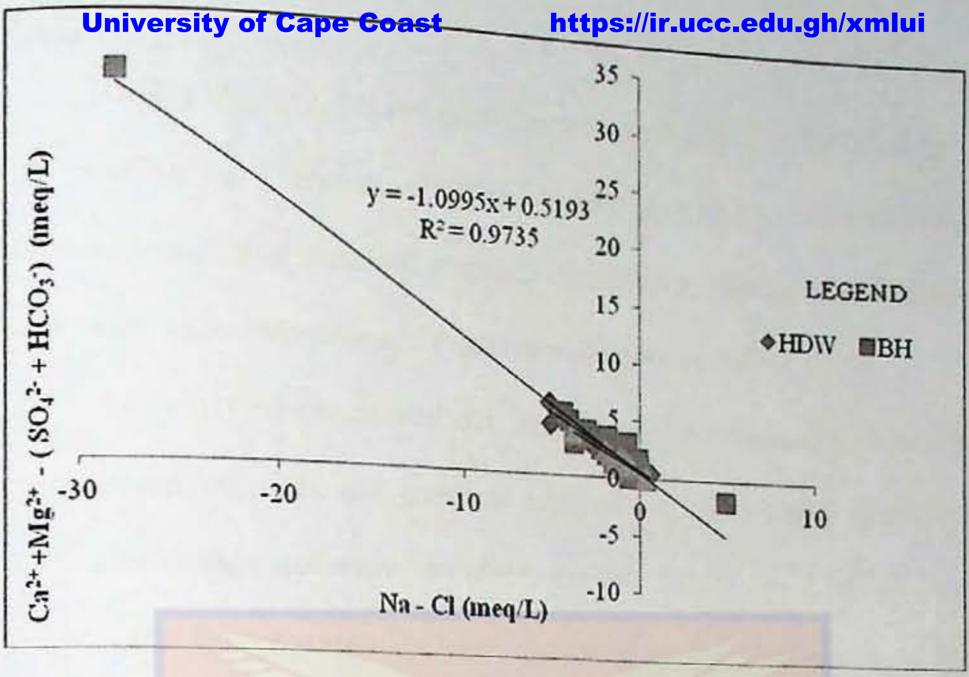

Figure 41: Relationship between ($Ca^{2+}$ + $Mg^{2+}$) – ($HCO_3^-$ + $SO_4^{2-}$) versus $Na^+$ - $Cl^-$ for the groundwater samples in the dry season.

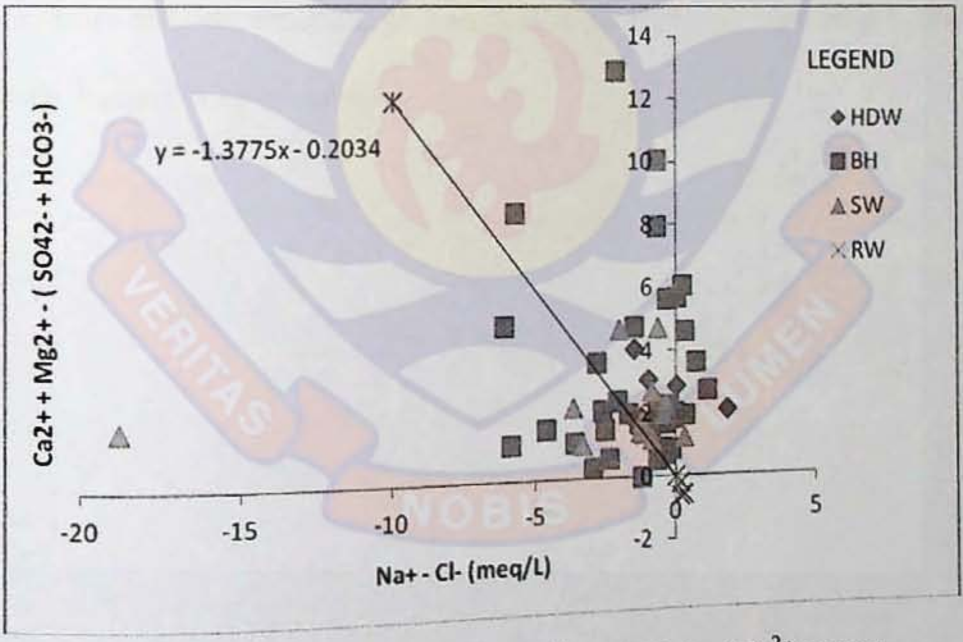

Figure 42: Relationship between $Ca^{2+}$ + $Mg^{2+}$ – ($HCO_3^-$ + $SO_4^{2-}$) versus $Na^+$ - $Cl^-$ for the groundwater samples in the rainy season.

### Gibbs Diagram

Gibb's diagrams that represent the ratios of $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3^-)$ as a function of TDS are widely employed to understand the functional sources of dissolved chemical constituents, such as precipitation-dominance, rock-dominance and evaporation dominance (Gibbs, 1970).

Gibbs (1970) has pointed out that the rate of evaporation, chemical compositions of rocks and chemical composition of rainwater generally control the chemistry of water. In order to evaluate the sources of various ions in the waters from Ayensu river basin, the chemical data for waters from the study area were plotted in Gibbs diagram (Figs.43 to 46). The data points on the Gibbs diagram, suggests that groundwater chemistry is controlled mainly by rock weathering and also to a very small extent evaporation in both the dry and rainy seasons during the study period. The evaporation process greatly increases the concentrations of ions formed by chemical weathering of the rock, leading to higher salinity.

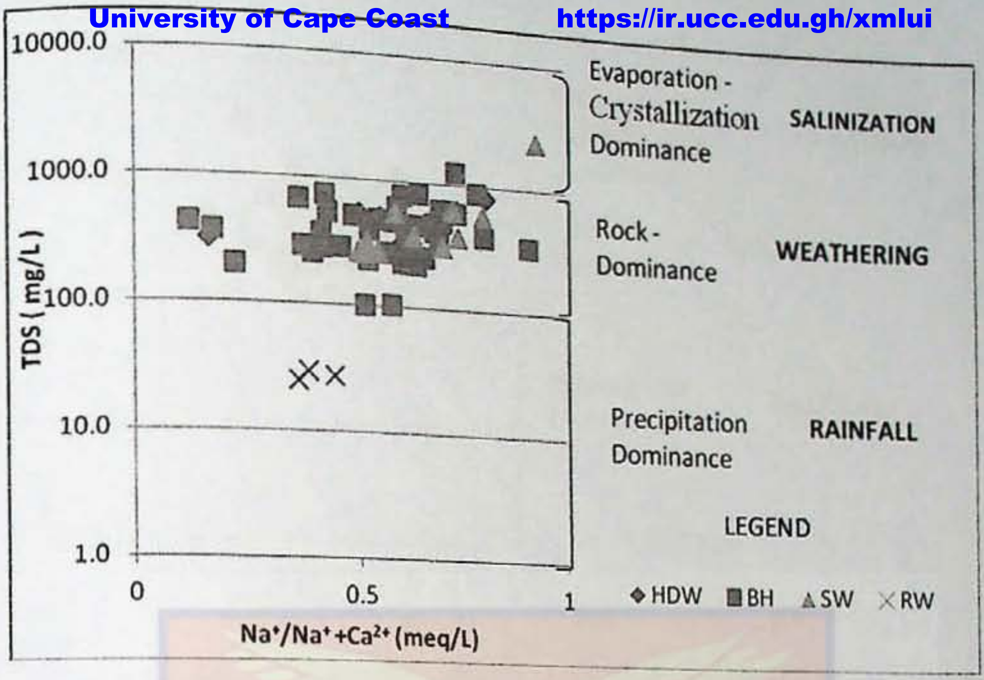

Figure 43: Gibb's Diagram: $Na^+ / Na^+ + Ca^{2+}$ as function of TDS showing some hydrochemical processes influencing groundwater chemical evolution for the rainy season.

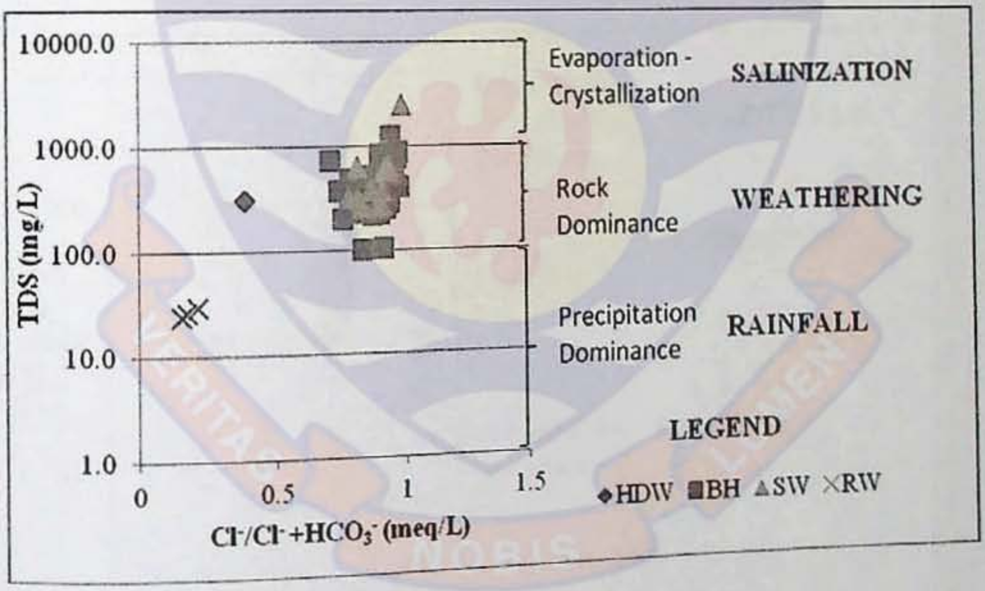

Figure 44: Gibb's Diagram: $Cl^- / Cl^- + HCO_3^-$ as function of TDS showing some hydrochemical processes influencing groundwater chemical evolution for the rainy season.

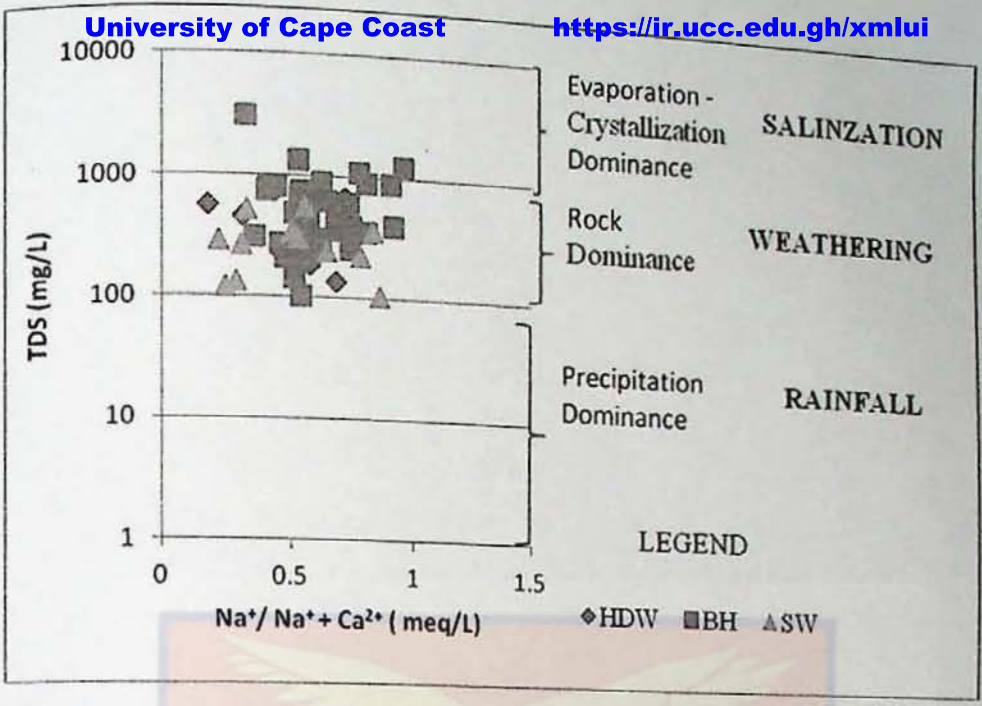

Figure 45: Gibb's Diagram: $Na^+ / Na^+ + Ca^{2+}$ as function of TDS showing some hydrochemical processes influencing groundwater chemical evolution for the dry season.

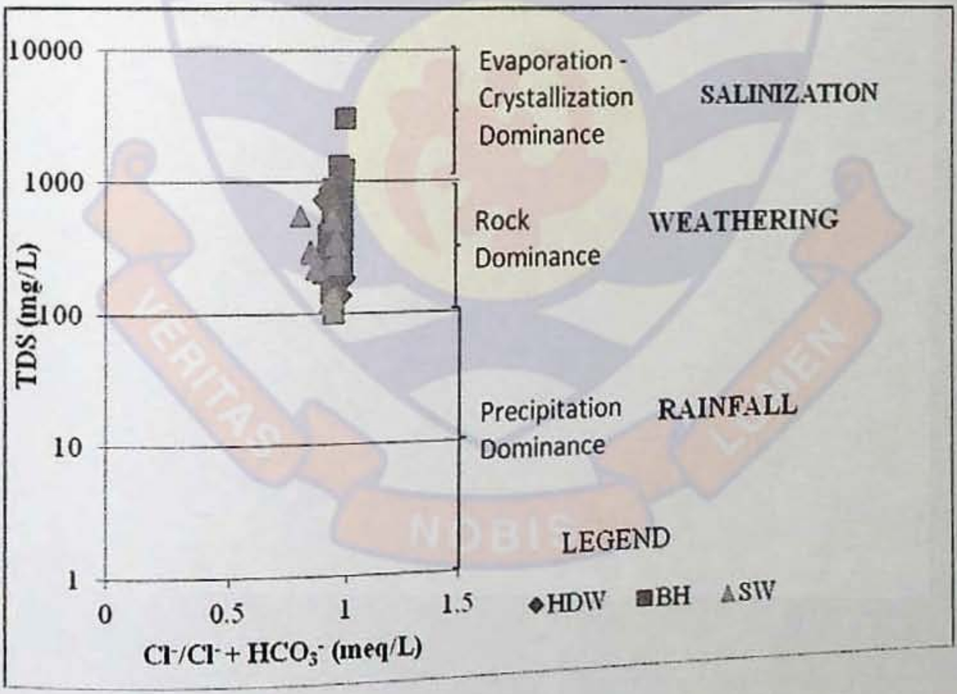

Figure 46: Gibb's Diagram: $Cl^- / Cl^- + HCO_3^-$ as function of TDS showing some hydrochemical processes influencing groundwater chemical evolution for the dry season

**Stable isotopes**

Analyses of $\delta^2H$ and $\delta^{18}O$ are used to identify the probable source of an underground water. The stable isotope data for deuterium ($\delta^2H$ ‰) and Oxygen - 18 ($\delta^{18}O$ ‰) are given in Table 28. The $\delta^2H$ values of the water samples range from -14.221‰ to 10.713‰ with a mean and median values of -5.04‰, and -6.04‰ respectively. The $\delta^{18}O$ values vary from -12.835‰ to 8.22‰ with a mean and median values of -1.91‰ and -2.15‰ respectively. The stable isotope data of $\delta^2H$ and $\delta^{18}O$ for the boreholes, hand dug wells, surface and rain waters are plotted in Fig. 47 together with the global meteoric water line (GMWL).

GMWL: $\delta^2H = 8.\delta^{18}O = 10$ (Craig, 1961).

Most of the water samples (including borehole, surface, hand dug well and rain waters) lie on or close to the GMWL suggesting recharge from meteoric origin. Thus recharge to the aquifer system in the Ayensu River Basin mainly come from local rainfall and slightly evaporated surface waters. Two of the surface waters (Dams at Gyehadze and Aduafokwa, with ($\delta^2HD$, $\delta^{18}O$) values of (9.54‰, 10.71‰) and (2.03‰, 1.00‰) respectively), plot below the GMWL indicating a degree of isotopic enrichment as a result of surface evaporation. These two dams are located in the sub-humid savannah zone of the Ayensu Basin and they were sampled in the dry season. Thus there was enough time for the stagnant waters to be subjected to intense evaporation. This indicates that heavy isotopes were enriched under a strong evaporation. A few groundwater, surface water and rainwater samples also showed evidence of isotopic enrichment by evaporation. Since evaporation may have taken place in these open wells under humid climatic conditions of the Ayensu Basin, the deviation from the Global Meteoric Water Line has not been as much pronounced as may have occurred under less humid climatic conditions (IAEA, 1983). Alternatively, the isotopic enrichment could be reflecting the integration of the isotopic composition of the various tributaries that take their sources from a relatively drier part of the country other than the Ayensu Basin (Kortatsi, 2007).

Table 28: Stable isotope data for groundwater, surfacewater (rivers and dams) and rainwater in the Ayensu river basin.

| Location | Type | Date | EC | T°C | $\delta^2$H(‰) | $\delta^{18}$O(‰) |
|---|---|---|---|---|---|---|
| Kanyanko | Borehole 1 | 31-05 -2011 | 1027.0 | 24.3 | -7.81 | -2.06 |
| Kanyanko | Borehole 2 | 31-05 -2011 | 682.1 | 24.5 | -8.21 | -2.34 |
| Osimpo | Borehole | 31-05 -2011 | 1290 | 27.0 | -4.65 | -1.54 |
| A.Kwabenya | Borehole 1 | 31-05 -2011 | 1312.0 | 23.3 | -4.29 | -1.42 |
| A. Kwabenya | Borehole 2 | 31-05 -2011 | 1303.0 | 22.4 | -7.53 | -1.74 |
| A. Kwabenya | Stream | 31-05 -2011 | 832.7 | 21.1 | -0.45 | -0.83 |
| Kokroabo | Borehole | 31-05 -2011 | 515.3 | 26.4 | -8.77 | -2.21 |
| Kweikrom | Borehole | 31-05 -2011 | 1256 | 23.9 | 0.59 | -0.85 |
| Amanfor | Borehole 2 | 31-05 -2011 | 987.1 | 24.2 | -8.21 | -2.34 |
| Obosomase | Borehole | 31-05 -2011 | 832.7 | 23.2 | -6.95 | -2.31 |
| Ojobi | Borehole | 31-05 -2011 | 1003.0 | 22.7 | -8.13 | -2.34 |
| Gyangyanadze | Borrehole | 31-05 -2011 | 2108.0 | 25.5 | -14.22 | -3.12 |
| Penin | Borehole 2 | 31-05 -2011 | 817.9 | 24.7 | -0.52 | -1.65 |
| M. Nkwanta | River | 31-05 -2011 | 225.4 | 25.4 | -6.63 | -2.35 |

Table 28 continued

| | | | | | | |
|---|---|---|---|---|---|---|
| Doato | Borehole 2 | 31-05 -2011 | 708.6 | 22.8 | -8.26 | -2.46 |
| Ofaso | Borehole | 31-05 -2011 | 1306.0 | 22.3 | -10.55 | -2.23 |
| Fianko | Borehole | 31-05 -2011 | 1081.0 | 23.2 | -5.11 | -1.75 |
| Penin | Stream | 31-05 -2011 | 483.9 | 22.5 | -6.68 | -2.43 |
| Kofikum | Borehole | 31-05-2011 | 414.4 | 28.5 | -6.02 | -2.26 |
| Namanwura | Borehole 1 | 31-05 -2011 | 525.9 | 26.3 | 0.83 | -1.31 |
| Obosomase | Stream | 31-05 -2011 | 695.5 | 22.5 | -0.45 | -0.83 |
| Ojobi | Pond | 31-05 -2011 | 1062.0 | 23.3 | -0.33 | -0.99 |
| Gyahadze | Dam | 31-05 -2011 | 592.7 | 25.4 | 9.54 | 2.03 |
| Bewadze | Borehole | 31-05 -2011 | 1588 | 28.5 | -6.06 | -1.72 |
| Osimpo | Stream | 31-05 -2011 | 483.6 | 23.4 | -4.41 | -1.05 |
| Oboyambo | Hand D. well | 31-05 -2011 | 166.4 | 27.8 | -7.41 | -1.62 |
| Topiase | Borehole | 31-05 -2011 | 2281.0 | 27.0 | -8.46 | -2.02 |
| A. Tekyeman | Borehole | 31-05 -2011 | 658.9 | 28.1 | -6.82 | -2.29 |
| Dankwaa | Borehole | 07-06 -2011 | 711.6 | 22.8 | -9.04 | -2.59 |
| Kweikrom | Hand D.well1 | 07-06 -2011 | 906.5 | 23.6 | -7.75 | -2.61 |
| Oboyambo | Borehole | 07-06 -2011 | 583.5 | 25.8 | -7.29 | -2.58 |
| Doato | Borehole | 07-05 -2011 | 433.9 | 24.0 | -7.71 | -2.31 |
| Alabra | Borehole | 07-06 -2011 | 981.2 | 28.7 | -11.78 | -2.74 |
| Kanyanko | Borehole 2 | 07-06 -2011 | 682.1 | 24.5 | -5.61 | -2.20 |
| Kokroko | Borehole | 07-06 -2011 | 872.2 | 26.8 | -7.99 | -2.84 |
| Ojobi | Spring | 07-06 -2011 | 174.4 | 23.4 | -3.57 | -2.16 |
| Penin | Borehole 1 | 07-06 -2011 | 1566.0 | 24.9 | -3.60 | -1.95 |
| Kwakwa | River | 07-06 -2011 | 289.7 | 23.5 | -1.54 | -1.62 |

Table 28 continued

| | | | | | | |
|---|---|---|---|---|---|---|
| Namanwura | Borehole 2 | 07-06 -2011 | 267.2 | 26.0 | -9.82 | -2.72 |
| Oboyambo | Hand D.well2 | 07-06 -2011 | 610.1 | 27.7 | -6.18 | -2.13 |
| Mensakwa | Borehole | 07-06 -2011 | 1557.0 | 23.3 | -8.00 | -2.36 |
| Amanfor | Borehole 1 | 07-06 -2011 | 890.7 | 23.9 | -8.72 | -2.50 |
| Bewadze | Borehole | 07-06 -2011 | 1588.0 | 28.5 | -7.15 | -1.91 |
| A. Kwabenya | Borehole 1 | 07-06 -2011 | 1312.0 | 23.3 | -9.11 | -2.28 |
| Ayensuako | Borehole | 07-06 -2011 | 723.6 | 25.6 | -4.29 | -1.42 |
| Kokoado | Borehole | 07-06 -2011 | 1824.0 | 24.4 | -7.61 | -2.53 |
| Aduafokwa | Dam | 07-06 2011 | 362.9 | 25.7 | 10.71 | 1.00 |
| Otabilkwaa | Borehole | 07-06 -2011 | 713.4 | 25.7 | -4.72 | -2.41 |
| F. Bawjwase | Borehole 1 | 07-06 -2011 | 1079 | 24.5 | -10.78 | -2.14 |
| Kweikrom | Hand D.well2 | 07-06 -2011 | 448.0 | 30.4 | -5.82 | -1.44 |
| Oboyanbo | Hand D.well3 | 07-06 -2011 | 464.6 | 27.4 | -3.03 | -1.43 |
| Brahabekume | Borehole | 07-06 -2011 | 4311.0 | 27.2 | -7.16 | -2.05 |
| Kwesikumkwa | Borehole | 07-06 -2011 | 336.2 | 25.3 | -2.55 | -1.19 |
| F. Bawjwase | Borehole 2 | 07-06 -2011 | 878.1 | 24.7 | -9.71 | -2.31 |
| Kyerebuakwa | Borehole | 07-06 -2011 | 678.7 | 24.8 | -7.45 | -2.48 |
| Dominase | Hand D.well | 07-06 -2011 | 1104.0 | 24.5 | -4.49 | -1.93 |
| Asabrekwaa | River | 07-06 -2011 | 635.6 | 23.1 | -1.44 | -1.45 |
| Kwanyako(Feb) | R.water | 07-06 -2011 | 107.9 | 29.3 | -0.61 | 6.32 |
| Kwanyako (March) | Rainwater | 07-06 -2011 | 68.34 | 28.9 | 0.33 | 2.13 |
| Kwanyako (May) | Rainwater | 07-07 -2011 | 38.33 | 29.1 | 0.30 | 8.22 |
| Swedru (March) | Rainwater | 07-06 -2011 | 70.59 | 29.0 | 0.64 | 3.63 |

Table 28 continued

| | | | | | | |
|---|---|---|---|---|---|---|
| Swedru (May) | Rainwater | 07-06 -2011 | 22.51 | 29.0 | 2.37 | 6.03 |
| Swedru (June) | Rainwater | 07-06 -2011 | 42.43 | 29.2 | 1.76 | 3.03 |
| Winneba (Jan) | Rainwater | 07-06 -2011 | 32.61 | 29.2 | 1.81 | 7.54 |
| Winneba (Feb) | Rainwater | 07-06 -2011 | 64.48 | 29.0 | 2.69 | 12.83 |
| Winneba (March) | Rainwater | 07-06 -2011 | 54.00 | 29.1 | 2.57 | 8.34 |
| Winneba (May) | Rainwater | 07-06 -2011 | 45.54 | 29.2 | 1.34 | 1.08 |

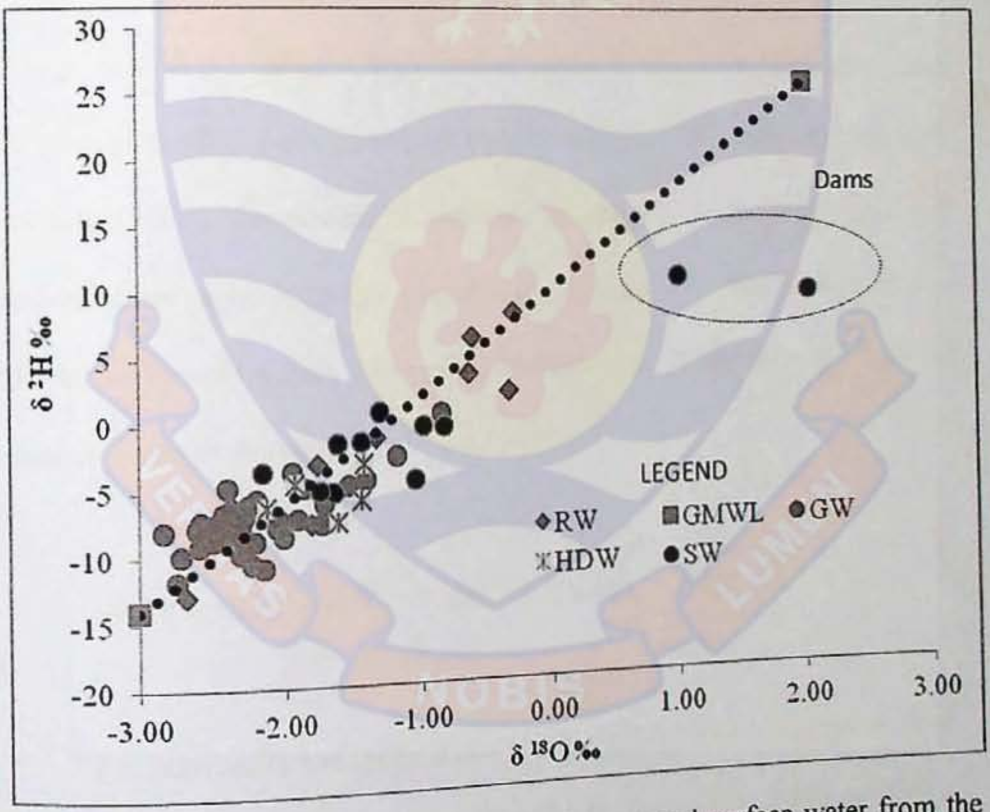

Figure 47: Isotopic composition of groundwaters and surface water from the Ayensu basin [ RW= Rain water, GW= Borehole, HDW= Hand dug well, SW= Surface water (river, dam &spring)].

### Minor and trace ions

During the dry season, aluminium, iron, and cadmium showed concentrations significantly above their detection limits in most of the water samples. Aluminium ion ($Al^{3+}$) varies in concentration in the groundwater samples from $< 0.030$ mg/L to 3.58 mg/L with a mean value of 1.74 mg/L and a median value of 2.044 mg/L. About 28% of the water samples had the $Al^{3+}$ ion concentrations below detection limit but approximately 43% of the samples had $Al^{3+}$ concentrations above the WHO maximum acceptable limit of 0.200 mg/L for drinking water (WHO, 2004). This will pose a risk of significant aesthetic problem to groundwater usage. Concentrations of $Al^{3+}$ in groundwater are strongly pH dependent (Nordstrom, 1982) and as expected boreholes with $pH < 6$ have high concentrations of $Al^{3+}$. However, some water samples with $pH > 7$ also have high concentrations of $Al^{3+}$ ions. According to Kortatsi (2007), dissolution of kaolinite or alunite , to provide extra acid neutralisation capacity to the groundwater, appears to be the main source of $Al^{3+}$ in the low pH waters. The typical kaolinite dissolution reaction in low pH water is given by the equation:

$$Al_2SiO_5(OH)_4 + 10H^+ \rightarrow 2Al^{3+} + 2H_2SiO_4 + 5H_2O$$

$Fe^{2+}$ concentration varies from $<0.006$ mg/L to 1.08 mg/L with a mean value of 0.659 mg/L and median value of 0.642 mg/L. Approximately 57% of the groundwater samples have their $Fe^{2+}$ concentration greater than the WHO guideline maximum value of 0.300 mg/L in drinking water, but an upper limit of 1.00 mg/L should suffice for most purposes (WHO, 2004; Kortatsi, 2007).

This does pose a major aesthetic problems to groundwater usage for domestic purposes in the Ayensu Basin. Oxidation and dissolution of pyrites and arsenopyrites should naturally be major sources of iron and sulphate ($SO_4^{2-}$) in the groundwaters (Kortatsi, 2007). However, there is no petrographic evidence that pyrites and arsenopyrites occur in the rock matrix in the Ayensu river basin. None of the water samples satisfy the iron to sulphate ($Fe^{2+}/SO_4^{2-}$) molar ratio of 0.5 and 1 for the stoichiometry of pyrite and arsenopyrite oxidation respectively. The ($Fe^{2+}/SO4^{2-}$) molar ratio ranges between 0.00 and 0.197 with a mean of 0.013 (Table 25.0). This suggests that pyrites and/or arsenopyrites oxidation cannot explain the high iron concentration in some of the groundwater samples.

The saturated indices of the iron species show that the waters are highly supersaturated with respect to geothite, hematite and $Fe(OH)_3$ (a). The supersaturation of the groundwater with respect to these iron-bearing minerals suggests that the groundwater has reacted with these minerals for long enough time to reach equilibrium and should be thermodynamically incapable of dissolving more of these iron species unless equilibrium conditions are changed. This means that the groundwater should be precipitating these iron minerals if it is oxygenated and therefore reducing the iron concentration in the boreholes (Kortatsi, 2007). However, this does not seem to be the case. As indicated by White and Yee (1985), $Fe^{3+}$ is reduced to $Fe^{2+}$ at the mineral surface. Geothite, hematite and magnetite are the main iron species present in the rock matrix within the study area. Iron may therefore, been derived from the reductive dissolution of hematite and to a limited extent magnetite in the presence of organic matter. The reduction is likely microbially mediated.

Hematite dissolution in the presence of protons (acid) is extremely slow. However, in the presence of organic ligands the reaction can be fast (Appelo & Postma, 1999). The presence of organic matter in the soil zone of the study area is indicated by the brown colouration of rivers and streams. An additional source of iron could be the leaching from ferromagnesian silicates, such as hornblende and pyroxenes (Kortatsi, 2007). This does pose major aesthetic problems to groundwater usage for domestic purposes in the Ayensu Basin. This problem can be solved by removing iron with filtration systems or by use of manganese sand to purify the water.

$Mn^{2+}$ concentration varies from < 0.002 mg/L to 0.561 mg/L with a mean value of 0.096 mg/L. Only two of the water samples in the Basin have $Mn^{2+}$ concentrations above the WHO permissible limit for portable water of 0.300 mg/L. Thus the manganese concentration in the groundwaters does not pose any major quality problem in the Ayensu river basin.

All the water samples have $Zn^{2+}$ concentration below the WHO recommended limit of 3.00 mg/L. $Cd^{2+}$ concentration, however, in 25% of the water samples are above the WHO maximum acceptable limit of 0.003 mg/L for drinking water (WHO, 2004). $Cd^{2+}$ concentration in the groundwater varies from <0.002mg/L (below detection limit) to 0.082 mg/L with a median value of 0.038 mg/L. This could pose serious health problems to the communities in which these boreholes occur. According to Stoeppler (1991) sources of $Cd^{2+}$ included wastes from Cd-based batteries, incinerators and run-off from agricultural soils where phosphate fertilizers are used since $Cd^{2+}$ is a common impurity in phosphate fertilizers. Some of these boreholes are located in or near cocoa farms where fertilizer are used in growing the cocoa plants and thus could be a possible source of $Cd^{2+}$.

$Cr^{3+}$ ion concentration in the water samples varies from <0.006mg/L to 1.01mg/L with mean and median values of 0.179 mg/L and 0.148 mg/L respectively. Approximately 37% of the water samples have $Cr^{3+}$ concentration exceeding the WHO limit of 0.050 mg/L. High levels of chromium could pose serious health problems.

In the rainy season of the study period most of the water samples in the Ayensu river basin have their trace metal concentrations below detection limits. However, some groundwaters have concentration levels of aluminum, iron and in few cases cadmium significantly above their detection levels. As was the case in the dry, these same ions ($Fe^{2+}$, $Al^{3+}$ and $Cd^{2+}$ ) had their concentration levels exceeding the WHO guideline limits for drinking water; 0.300 mg/L, 0.200 mg/L and 0.003 mg/L respectively. This indicates that the seasonal variations have only a slight impact on the spatial variability of the hydrochemistry in the Ayensu river basin.

# CHAPTER FIVE

# CONCLUSION AND RECOMMENDATIONS

## CONCLUSION

Analysis of the hydrochemical survey data from the study area revealed that the groundwater is mildly acidic ( 4.77 - 7.44) in the dry season and in the rainy season the pH is between 4.9 - 7.80. All the surface waters (rivers, streams and dams) had pH values greater than 7. In the dry season 6.7% (Four boreholes at Gyangyanadze, Brahabekume, Topiase and Aduafokwa), had their Total Dissolved Solids (TDS) values above 1000mg/L which are considered high salinity waters. Only two of the boreholes (Topiase and Brahabekume ) had their TDS values above 1000mg/L during the rainy season. The rest of the water samples in the Ayensu basin had TDS values below 1000 mg/L, WHO recommended value for domestic water, which are classified as fresh water. There were no seasonal trends observed in total dissolved solids (TDS) from the boreholes sampled over the sampling period.

## Water Types

Three major water types have been delineated using the phase diagrams. The three types are Na -Cl, Ca- Mg- Cl and Ca- Mg- SO4 waters. Most of the groundwaters cluster toward the Na - Cl facie during the rainy and dry seasons. The surface waters and a few of the boreholes and hand dug wells show the Ca - Mg - Cl and Ca - Mg - SO4 water types during the dry season, but in the rainy season, most of the surface waters and the hand dug wells plot mainly in the mixed water section where there is neither dominant cation or anion.

During both the dry and rainy seasons, $Na^+$ showed a clear dominance over all the major cations; 63.3% and 72% of all the water samples in the dry and rainy seasons respectively. In few water samples, $Ca^{2+}$ or $Mg^{2+}$ appear to be the dominant cation in both seasons. The dominant anion in the groundwaters in the Ayensu River Basin during the study period was $Cl^-$ followed by $SO_4^{2-}$, $HCO_3^-$, $NO_3^-$ and $PO_4^{3-}$. During the dry season, (8 boreholes), 13.3% of the water samples exceeded the permissible levels of 250mg/L for $Cl^-$ ion. For the rainy season, 16.7% (10 boreholes) had their $Cl^-$ ion concentration exceeding the WHO permissible level. Approximately 27% of the groundwater samples had their $NO_3^-$ concentrations exceeding the WHO maximum acceptable limit of 50 mg/l in the rainy season. This may cause health problems for infants using such waters as source of drinking water. During the dry season all the $NO_3^-$ values were blow the WHO acceptable limit.

## Trace Metals

The trace metal loading of the groundwater is not high. During the dry season, aluminium, iron, and cadmium showed concentrations significantly above their detection limits in most of the water samples. Some of the water samples had the $\mathrm{Al}^{3+}$ ion concentrations below detection limit but approximately 43% of the samples had $\mathrm{Al}^{3+}$ concentrations above the WHO maximum acceptable limit of 0.200 mg/l for drinking water.

Approximately, 57% of the groundwater samples had their $\mathrm{Fe}^{2+}$ concentration greater than the WHO guideline maximum value of 0.300 mg/l in drinking water, but an upper limit of 1.00 mg/L should suffice for most purposes. Some of the water samples (25%) have $\mathrm{Cd}^{2+}$ concentration above the WHO maximum acceptable limit of 0.003 mg/L for drinking water. $\mathrm{Al}^{3+}$, $\mathrm{Fe}^{2+}$ and $\mathrm{Cd}^{2+}$ show the same trend during the rainy season by having their concentration level above the WHO permissible limits for portable water.

## Groundwater quality

The groundwater in the study area is undersaturated with respect to the common carbonates (calcite. aragonite and dolomite). The data points on the Gibbs diagrams (Fig.12- Fig.15) suggest that, groundwater chemistry of the Ayensu River Basin is controlled mainly by rock weathering and also to a very small extent by evaporation in both the dry and rainy seasons. The evaporation process greatly increases the concentrations of ions formed by chemical weathering of the rock, leading to higher salinity. Cation exchange and reverse ion exchange are also some of the hydrogeochemical processes controlling the groundwater chemistry in the study area.

## Stable Isotopes

From the stable isotope data for deuterium ($\delta^2H$ ‰) and Oxygen - 18 ($\delta^{18}O$ ‰) of the study area it is concluded that recharge to the aquifer system in the Ayensu River Basin mainly come from local rainfall and slightly evaporated surface waters.

## RECOMMENDATIONS

1. Tritium and Carbon-14 contents of the groundwaters should be determined to estimate the age or residence time of the waters.
2. Above and beyond the high salinities obtained in certain boreholes, the groundwaters in the area do not appear to pose an immediate and direct threat to human health. However, a monitoring programme should be employed to monitor for future groundwater pollution.
3. More anions such as Br-, F- etc should be determined along with other trace metals that were not analysed in this study.

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# List of Abbreviations

**WHO:** World Health Organisation

**IAEA:** International Atomic Energy Agency

**FAO:** Food and Agriculture Organisation

**UN:** United Nations

**ATSDR**: (Agency for toxic substances and Disease Registry)

**APHA:** American Public Health Association

**AWWA**: American Water Works Association

**WEF**: Water Environment Federation

**Appendix 1. The sampling sites and their coordinates and the type of facilities available.**

| No. | WELL No./TYPE | LOCATION | GPS | |
|---|---|---|---|---|
| 1 | BOREHOLE | OJOBI | N 050 28.989' | W00032.198' |
| 2 | HAND DUG WELL | OJOBI | N 050 29.059' | W00032.178' |
| 3 | POND | OJOBI | N 050 29.037 | W00032.197' |
| 4 | SPRING | OJOBI | N 050 29.193' | W000 32.343' |
| 5 | 032/C/94-3(BH) | KWEIKROM | N 050 25.249' | W00033.499' |
| 6 | HAND DUG WELL1 | KWEIKROM | N 050 25.253' | W00033.497' |
| 7 | HAND DUG WELL2 | KWEIKROM | N 050 25.282' | W00033.489 |
| 8 | 210-BU3(BH) | GYANGYANNADZE | N 050 23.921' | W00034.542' |
| 9 | DAM | GYEHADZE | N 050 23.243' | W00035.368' |
| 10 | RIVER AYENSU | ADAWUKWA | N 050 25.038' | W00036.600' |
| 11 | RIVER AYENSU | ADAWUKWA | N 050 25.215' | W00036.412' |
| 12 | HAND DUG WELL | DOMINASE | N 050 29.055' | W00035.552' |
| 13 | 617-BU1(BH) | A. KWABENYA | N 050 42.435' | W00032.254' |
| 14 | 609-BU1(BH) | A. KWABENYA | N 050 42.415' | W00032.303' |
| 15 | STREAM | A. KWABENYA | N 050 42.475' | W000 32.333' |
| 16 | 620-BU1(BH) | OFASO | N 050 42.896' | W00033.536' |
| 17 | 613-BU1(BH) | DANKWA | N 050 42.613' | W000 31.588' |
| 18 | 56-C47-1(BH) | FIANKOO | N 050 43.186' | W000 31.634' |
| 19 | 603-BU1 | PENIN | N 050 42.472' | W000 35.446' |
| 20 | 131-BU2(BH) | PENIN | N 050 42.429' | W000 35.391' |
| 21 | STREAM | PENIN | N 050 42.434' | W000 35.384' |
| 22 | 601-BU1(BH) | OSIMPO | N 050 42.830' | W000 36.947' |
| 23 | RIVER ARKU | OSIMPO | N 050 42.799' | W000 36.928' |
| 24 | 056/B/47-4 | AYENSUAKO | N 050 42.713' | W000 36.917' |
| 25 | 596-BU1(BH) | TEKYEMAN | N 050 41.797' | W000 36.979' |
| 26 | RIVER AYENSU | KWAKWA | N 050 40.882' | W000 37.459' |
| 27 | RIVER AYENSU | M, NKWANTA | N 050 38.563' | W000 36.730' |
| 28 | STREAM | OBOSOMASE | N 050 64.254' | W000.635790 |
| 29 | 563-BU1(BH) | OBOSOMASE | N 050 38.516' | W000338.131 |
| 30 | 351-BU1(BH) | KOKOADO | N 050 65.441' | W000.63579 |
| 31 | 592-BU1 | MENSAKWAA | N 050 39.499 | W00038.922 |
| 32 | 553-BU1(BH) | ESELKWAA | N 05 66.256' | W000.64324 |
| 33 | 569-BU1 | AMANFOR | N 050 38.118 | W00039.834 |
| 34 | 557-BU1 | AMANFOR | N 050 3551' | W004306 |
| 35 | 525-BU1(BH) | NAMONWURA | N 05.64117 | W000.67368 |
| 36 | 143-BU3(BH) | NAMONWURA | N 0538.604 | W0040.456 |
| 37 | 144-BU2(BH) | OHIAWOANWU | N 05.63656 | W000.68628 |
| 38 | 559-BU1(BH) | OTABILKWAA | N 05.63541 | W000.69138 |

Appendix1 continued

| | | | | |
|---|---|---|---|---|
| 39 | 128-BU3 (BH) | KWESIKUMKWAA | N 05.67182 | W000.71699 |
| 40 | 129-BU3 (BH) | DOATO | N 05.68942 | W000.68948 |
| 41 | 496-BU1 (BH) | DOATO | N 05.68799 | W000.68646 |
| 42 | 497-BU1(BH) | KANYANKO | N 05.69099 | W000.67058 |
| 43 | 198-BU1 (BH) | KANYANKO | N 05.69256 | W000.66879 |
| 44 | 560-BU1 (BH 1) | FANTE BAWJOASE | N 05.66878 | W000.65247 |
| 45 | 562-BU1 (BH 2) | FANTE BAWJOASE | N 05.68814 | W000.64995 |
| 46 | 568-BU1 (BH) | KOFIKUM | N 05.70764 | W000.63860 |
| 47 | HAND DUG WELL1 | OBOYAMBO | N 05.71003 | W000.65376 |
| 48 | 580-BU1 (BH) | OBOYAMBO | N 05.71080 | W000.65326 |
| 49 | HAND DUG WELL2 | OBOYAMBO | N 05.71180 | W000.65305 |
| 50 | HAND DUG w. 3 | OBOYAMBO | N 05.71181 | W000.65258 |
| 51 | 564-BU1 (BH) | OKAEKROM | N 05.68735 | W000.64147 |
| 52 | 589-BU1 (BH) | BEWADZE | N 05.57286 | W000.59511 |
| 53 | 585-BU1 (BH) | ADUAFOKWA | N 05.55712 | W000.57170 |
| 54 | 204-BU3 (BH) | ALABRA | N 05.55041 | W000.57468 |
| 55 | 136-BU2 (BH) | TOPIASE.NO.2 | N 0538.742 | W0037.923 |
| 56 | BOREHOLE | BRAHABEKUME | N 0531.437 | W0040.127 |
| 57 | 146-BU2 (BH) | KYEREBUKWA | N 0539.035 | W0040.640 |
| 58 | 153-BU2 (BH) | KOKROKO | N 054.013 | W 0039.18 |

**Appendix 2: Physico-chemical parameters, major and minor constituents and charge balance error in percentage (CBE%) for the Dry Season.**

| Location | Type | pH | ToC | EC | TDS | SAL | ALK | Ca | Mg | Na | K | Cl | SO4 | HCO3 | NO3 | PO43 | CBE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ojobi | | 6.74 | 27.6 | 1482 | 815.0 | 0.89 | 26.7 | 83.25 | 12.15 | 378.50 | 8.80 | 518.28 | 207.36 | 32.51 | 31.75 | 0.504 | 4.49 |
| Ojobi | | 6.99 | 27.4 | 1033.8 | 570.1 | 0.62 | 80.0 | 78.6 | 16.36 | 110.0 | 9.75 | 213.0 | 77.369 | 97.6 | 89.58 | 5.09 | -2.3 |
| Ojobi | POND | 6.37 | 27.9 | 978.9 | 536.50 | 0.58 | 6.57 | 35.62 | 8.02 | 65.00 | 3.50 | 112.34 | 57.3 | 8.02 | 9.099 | 1.68 | 6.72 |
| Ojobi | SPRING | 6.59 | 27.8 | 576.4 | 313.3 | 0.35 | 12.5 | 4.80 | 7.80 | 19.70 | 6.00 | 29.46 | 31.72 | 15.25 | 1.91 | <0.001 | 3.51 |
| Kweikrom | BH | 6.42 | BH | 1132.8 | 616.2 | 0.66 | 32.0 | 57.20 | 22.53 | 120.00 | 4.20 | 220.1 | 67.78 | 39.04 | 33.53 | <0.001 | .73 |
| Kweikrom | HDW1 | 7.80 | HDW | 1270 | 512.8 | 0.52 | 40.0 | 42.80 | 24.3 | 52.00 | 4.60 | 108.8 | 70.78 | 48.8 | 10.50 | 0.68 | .4 |
| Kweikrom | HDW2 | 6.78 | 26.8 | 1321.0 | 291.5 | 0.52 | 24.2 | 56.40 | 13.6 | 88.0 | 15.00 | 189.0 | 81.9 | 29.52 | 2.00 | 0.68 | 3.79 |
| GYAN | BH | 7.27 | 28.7 | 1639.5 | 869.2 | 0.97 | 32.3 | 146.96 | 29.56 | 343.0 | 8.40 | 633.55 | 169.17 | 39.36 | 4.143 | 0.60 | 6.03 |
| Gyehadze | DAM | 7.74 | 31.7 | 888.2 | 489.7 | 0.50 | 19.8 | 48.0 | 30.2 | 79.0 | 18.0 | 81.71 | 109.0 | 24.2 | 223.9 | 2.06 | 0.96 |
| Adawukwa | RIVER | 8.2 | 28.2 | 674.8 | 367.2 | 0.41 | 44.0 | 41.0 | 7.8 | 34.1 | 9.1 | 64.5 | 31.319 | 53.68 | 57.41 | 0.212 | 1.5 |
| Adawukwa | RIVER | 7.95 | 29.1 | 654.9 | 735.5 | 0.48 | 52.0 | 39.0 | 26.5 | 36.0 | 4.6 | 102.0 | 44.6 | 78.08 | 14.8 | 0.34 | 4.5 |
| Dominase | HDW | 7.93 | 27.3 | 1053.5 | 585.9 | 0.64 | 66.6 | 90.1 | 29.16 | 112.0 | 4.4 | 159.75 | 132.195 | 81.2 | 85.98 | 1.11 | 8.71 |
| Mankrong-N | RIVER | 7.87 | 27.6 | 776.1 | 423.4 | 0.46 | 34.4 | 14.98 | 23.6 | 9.0 | 3.5 | 66.29 | 28.262 | 42.0 | 2.287 | <0.001 | 0.24 |
| Kwakwa | RIVER | 8.28 | 27.2 | 364 | 198.2 | 0.20 | 26.9 | 42.4 | 5.65 | 38.4 | 5.7 | 84.0 | 48.03 | 32.8 | 2.287 | <0.001 | 5.57 |
| Ag.Tekyeman | BH | 5.47 | 28.2 | 744.1 | 406.3 | 0.44 | 59.8 | 42.9 | 23.67 | 102.0 | 12.2 | 131.3 | 56.987 | 73.0 | 117.9 | 0.767 | 5.08 |
| Ayensuako | BH | 7.17 | 27.9 | 939.3 | 510.8 | 0.56 | 18.3 | 35.3 | 16.2 | 100.4 | 15 | 146.3 | 40.137 | 22.36 | 100.6 | 2.218 | 5.7 |
| Osimpo | BH | 6.34 | 27.9 | 826.95 | 450.6 | 0.50 | 25.5 | 59.7 | 47.5 | 106.5 | 4.1 | 263.66 | 79.385 | 31.11 | 109.4 | <0.001 | 1.38 |
| Osimpo | STREAM | 6.03 | 27.1 | 413.7 | 226.1 | 0.232 | 32.0 | 43.4 | 13.77 | 72.0 | 4.3 | 127.8 | 39.85 | 39.04 | 79.3 | 0.282 | 1.55 |
| Penin | BH1 | 5.97 | 27.9 | 1404.5 | 778.3 | 0.886 | 38.91 | 121.8 | 66.25 | 107.0 | 19 | 382.36 | 139.618 | 47.47 | 104.9 | 1.029 | 1.73 |
| Penin | BH2 | 5.82 | 27.7 | 977.6 | 533.7 | 0.589 | 33.9 | 56.24 | 42.6 | 85.55 | 8.85 | 209.01 | 98.589 | 41.36 | 126.4 | 0.225 | -1.7 |
| Penin | STREAM | 6.19 | 27 | 884.8 | 480.7 | 0.531 | 31.7 | 40.3 | 22.4 | 51.0 | 2.5 | 123.07 | 48.33 | 38.68 | 15.04 | <0.001 | 7.06 |
| A.kwabenya | BH1 | 6.92 | 28.1 | 1233 | 663.3 | 0.722 | 36.0 | 92 | 47.39 | 64.0 | 8.2 | 302.5 | 85.138 | 43.92 | 155.3 | <0.001 | -7.9 |

Appendix 2
continued

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| A.kwabenya | BH2 | 6.7 | 29.7 | 1141 | 623.8 | 0.692 | 36.7 | 52 | 37.6 | 79.0 | 10.6 | 206.0 | 64.48 | 44.77 | 39.38 | 0.61 | 5.04 |
| A.kwabenya | STREAM | 7.86 | 26.3 | 521.9 | 285.4 | 0.296 | 50.9 | 55.11 | 43.44 | 23.0 | 1.5 | 199.0 | 30.05 | 62.1 | 0.271 | <0.001 | 1.09 |
| Dankwa | BH | 6.34 | 26.9 | 878.8 | 476.5 | 0.523 | 19.8 | 41.23 | 6.05 | 100.6 | 4.1 | 166.75 | 60.82 | 24.16 | 26.18 | 0.181 | 1.72 |
| Fianko | BH | 5.94 | 27.1 | 1110.5 | 603.7 | 0.666 | 19.4 | 61.29 | 46.49 | 115.6 | 4.2 | 251.7 | 79.385 | 23.67 | 109.4 | 0.365 | 5.12 |
| Ofaso | BH | 6.6 | 21.6 | 917.2 | 498.8 | 0.575 | 19.15 | 100 | 121.7 | 102.2 | 1.5 | 250.0 | 89.943 | 23.36 | 1.276 | <0.001 | 35.6 |
| Obosomase | BH | 5.89 | 26.3 | 517.1 | 283.2 | 0.318 | 17.86 | 32 | 20 | 32.0 | 4.4 | 89.215 | 60.341 | 21.79 | 9.199 | 8.383 | 2.47 |
| Obosomase | STREAM | 6.48 | 27 | 424.8 | 230.8 | 0.257 | 37.9 | 37.35 | 22.7 | 60.8 | 9.6 | 115.9 | 85 | 46.24 | 23.2 | 2.705 | 3.07 |
| Topiase | BH | 5.52 | 27 | 2281 | 1251 | 1.432 | 20.0 | 98.6 | 66 | 125.5 | 15.6 | 402.3 | 76.861 | 24.4 | 23.6 | <0.001 | 8.57 |
| Mensakwa | BH | 5.64 | 26.8 | 1146 | 626.1 | 0.73 | 27.8 | 47.7 | 10.6 | 102.0 | 9.2 | 180.13 | 100.41 | 33.92 | <0.001 | <0.001 | 1.39 |
| Esselkwa | BH | 5.68 | 28.7 | 737.8 | 406.9 | 0.465 | 19.12 | 34.3 | 24.7 | 81.0 | 5.3 | 137.82 | 87.4 | 23.32 | <0.001 | 17.75 | 5.58 |
| Amanfor | BH1 | 5.78 | 27.3 | 641.6 | 350.7 | 0.397 | 24.0 | 41 | 32.4 | 67.0 | 3.7 | 123.48 | 104.18 | 29.28 | 25.74 | 1.324 | 8.17 |
| Amanfor | BH2 | 5.56 | 27.3 | 987.1 | 389.9 | 0.388 | 28.0 | 42.6 | 31.3 | 51.0 | 5.2 | 169.0 | 84.2 | 34.16 | 6.743 | 3.5 | -1.4 |
| Namonwura | BH1 | 5.81 | 27.8 | 191.1 | 102.8 | 0.11 | 24.82 | 38.05 | 24.6 | 53.0 | 7.8 | 118.3 | 63.5 | 30.27 | 9.557 | <0.001 | 9.79 |
| Namonwura | BH2 | 5.92 | 26 | 367.2 | 100 | 0.221 | 32.0 | 33 | 25.3 | 51.5 | 6.7 | 85.301 | 68.0 | 39.04 | 40.96 | <0.001 | 9.29 |
| Kokoado | BH | 5.85 | 28.7 | 1824 | 815 | 0.819 | 44.0 | 48.6 | 43.5 | 94.5 | 9.8 | 154.0 | 214.0 | 53.68 | 0.154 | 2.45 | 3.27 |
| Kyerebuakwa | BH | 7.54 | 27.6 | 362.6 | 316.4 | 0.195 | 35.2 | 40 | 32.46 | 62.0 | 9.4 | 97.5 | 137.0 | 42.95 | 41.49 | <0.001 | 4.57 |
| Ohiawoawu | BH | 5.37 | 27.9 | 404.4 | 220.6 | 0.245 | 25.15 | 38.95 | 13.3 | 69.0 | 7.2 | 96.06 | 98.47 | 30.68 | 20.37 | 2.347 | 4.85 |
| Otabilkwa | BH | 5.34 | 28.3 | 469.2 | 254.8 | 0.286 | 13.52 | 33 | 22.7 | 84.6 | 13.9 | 131.59 | 77.5 | 16.5 | 44.88 | <0.001 | 9.07 |
| Kwesikumkwa | BH | 5.77 | 27.4 | 292 | 267.7 | 0.138 | 21.12 | 26 | 21.8 | 49.5 | 4.2 | 117.18 | 35.0 | 25.74 | 15.88 | 0.239 | 6.55 |
| Doato | BH1 | 5.53 | 28 | 470.5 | 256.8 | 0.288 | 25.1 | 28 | 23 | 53.0 | 11.8 | 113.63 | 63.5 | 30.62 | 10.72 | 0.532 | 8.03 |
| Doato | BH2 | 5.63 | 27.15 | 359 | 255.1 | 0.154 | 16.0 | 34 | 23 | 47.0 | 5.4 | 96.7 | 87.06 | 19.52 | 5.724 | 0.532 | 8.66 |
| Kanyanko | BH1 | 5.6 | 28.1 | 662.7 | 365.6 | 0.417 | 24.0 | 42.4 | 8.4 | 73.0 | 9.9 | 112.26 | 72.4 | 29.28 | 6.34 | <0.001 | 8.65 |

Appendix 2 continued

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Kanyanko | BH2 | 5.32 | 28.3 | 518.1 | 278.4 | 0.312 | 24.0 | 45.7 | 22.5 | 27.0 | 11.4 | 102.0 | 69.58 | 29.28 | 4.243 | <0.001 | 7.9 |
| Okaekrom | BH | 6.74 | 26.2 | 717.6 | 393.8 | 0.452 | 16.0 | 33.3 | 26.5 | 133.0 | 3.4 | 218.0 | 82.5 | 19.52 | 4.557 | 0.321 | 5.45 |
| F.Bawjoase | BH1 | 7 | 24.4 | 728.6 | 399.8 | 0.459 | 20.0 | 34.45 | 47.4 | 45.0 | 4.6 | 197.85 | 33.21 | 24.4 | 33.91 | 0.869 | 5.78 |
| F.Bawjoase | BH2 | 6.05 | 24.1 | 611.5 | 337.7 | 0.383 | 16.0 | 38.4 | 22.6 | 56.0 | 7.1 | 128.56 | 71.8 | 19.52 | 12.91 | 0.703 | 8.09 |
| Kofikumkwa | BH | 6.96 | 26.2 | 481.3 | 262.8 | 0.294 | 32.0 | 33.2 | 21.7 | 66.0 | 5.7 | 114.5 | 69.4 | 39.04 | 16.32 | 0.412 | 7.43 |
| Oboyambo | BH | 5.72 | 25.8 | 583.5 | 322.6 | 0.365 | 16.6 | 28.7 | 22.6 | 51.0 | 4.4 | 109.1 | 67.5 | 20.25 | 12.56 | 0.27 | 5.87 |
| Oboyambo | HDW1 | 7.58 | 26.1 | 1133 | 622.3 | 0.727 | 28.6 | 37.7 | 40.33 | 118.7 | 6.8 | 198.45 | 77.39 | 34.89 | 60.37 | 0.545 | 9.39 |
| Oboyambo | HDW2 | 6.53 | 27.9 | 506 | 314 | 0.163 | 28.0 | 37.15 | 31 | 40.0 | 7.3 | 106.5 | 67.18 | 34.16 | 24.35 | 0.735 | 8.44 |
| Oboyambo | HDW3 | 7.85 | 28.1 | 429 | 266 | 0.236 | 24.0 | 53 | 31.55 | 48.2 | 3.4 | 192.6 | 35.2 | 29.28 | 86.8 | 0.555 | -3.8 |
| Brahabekume | BH | 7.25 | 27.2 | 4311 | 2430 | 3.035 | 38.0 | 63.6 | 192.9 | 656.0 | 53 | 1680.1 | 406.0 | 46.36 | 25.04 | <0.001 | -7.4 |
| Alabra | BH | 6.59 | 27 | 1145.5 | 627 | 0.689 | 25.2 | 90.1 | 47.65 | 120.0 | 4.35 | 315.07 | 109.426 | 30.74 | 16.8 | 0.578 | 7.21 |
| Bewadze | BH | 6.27 | 25.4 | 1057 | 574.1 | 0.667 | 27.3 | 33.33 | 57.8 | 247.5 | 15.3 | 405.52 | 189.706 | 33.31 | 5.994 | <0.001 | 4.81 |
| Aduafokwa | BH | 7.27 | 27.4 | 712.8 | 385.3 | 0.43 | 30.2 | 28.9 | 24.6 | 120.0 | 2.0 | 174.0 | 106.0 | 36.84 | 16 | <0.001 | 4.73 |
| Asabrekwa | RIVER | 6.14 | 28.7 | 427.6 | 369.8 | 0.228 | 20.0 | 31.45 | 20.4 | 62.0 | 10.0 | 139.0 | 56.2 | 24.4 | 0.101 | 0.234 | 6.22 |
| Kokroko | BH | 4.9 | 25.5 | 872.2 | 567 | 0.877 | 23.0 | 54.2 | 42.68 | 88.0 | 4.9 | 208.0 | 53.8 | 28.06 | 69.08 | 0.545 | 8.77 |
| Kokroabo | BH | 5.36 | 26.1 | 344.4 | 258 | 0.184 | 28.0 | 34 | 32.6 | 41.0 | 3.3 | 93.6 | 56.1 | 34.16 | 62.35 | 1.03 | 7.53 |
| Winneba | RW | 7.38 | 29.2 | 49.16 | 24.635 | 0.022 | 13.02 | 8.0 | 2.00 | 5.1 | 5.2 | 3.0 | 19.175 | 13.02 | 0.511 | 0.00 | 2.96 |
| Swedru | RW | 7.45 | 29.1 | 62.78 | 26.941 | 0.023 | 20.0 | 10.0 | 1.00 | 9.1 | 13.1 | 6.45 | 24.3 | 24.4 | 1.01 | 0.00 | 0.00 |
| Kwanyako | RW | 7.05 | 29.1 | 62.83 | 29.545 | 0.025 | 16.0 | 9.0 | 3.00 | 6.35 | 19.55 | 6.57 | 32.6 | 19.52 | 0.998 | 0.00 | 0.98 |

## Appendix 3: Physico-chemical parameters, major and minor constituents and charge balance error in percentage (CBE%) for the Rainy Season.

| Location | Type | pH | ToC | EC | TDS | Sal | Alka | Ca | Mg | Na | K | Cl | SO4 | HCO3 | NO3 | PO4 | CBE |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ojobi | BH | 7.16 | 25.15 | 1680.7 | 883.77 | 0.932 | 13.60 | 26.5 | 62.69 | 305.0 | 10.30 | 497.6 | 153.0 | 16.59 | 1.20 | 0.76 | 6.8 |
| Ojobi | HDW | 7.44 | 25.45 | 1479.0 | 681.3 | 0.660 | 18.60 | 66.40 | 8.95 | 140.0 | 7.20 | 208.9 | 153.0 | 22.69 | 0.374 | 3.38 | 3.9 |
| Ojobi | POND | 7.62 | 26.1 | 1011.0 | 557.53 | 0.570 | 18.00 | 28.8 | 8.02 | 42.0 | 6.50 | 50.13 | 87.82 | 21.96 | 1.80 | 1.03 | 5.6 |
| Ojobi | Spring | 6.06 | 26.3 | 210.85 | 104.3 | 0.104 | 5.50 | 7.20 | 1.46 | 51.80 | 1.50 | 67.5 | 7.910 | 6.71 | 17.00 | 0.94 | 5.6 |
| Kweikrom | BH | 6.74 | 26.2 | 1334.7 | 717.6 | 0.747 | 6.80 | 50.4 | 15.10 | 92.5 | 4.20 | 230.38 | 20.48 | 8.30 | 2.80 | <0.001 | 5.4 |
| Kweikrom | HDW1 | 7.20 | 26.6 | 1042.7 | 565.37 | 0.583 | 12.80 | 99.20 | 24.3 | 24.00 | 10.40 | 220.1 | 23.330 | 15.62 | 1.80 | 0.42 | 8.6 |
| Kweikrom | HDW2 | 6.79 | 30.4 | 1009.3 | 454.4 | 0.441 | 24.60 | 112.0 | 10.6 | 59.0 | 4.90 | 272.46 | 73.33 | 30.01 | 0.105 | 0.21 | -2.8 |
| GYAN | BH | 7.73 | 27.65 | 2313.3 | 1247.0 | 1.333 | 15.10 | 18.55 | 74.73 | 510.5 | 7.70 | 613.9 | 416.97 | 18.44 | 0.186 | 0.14 | 5.8 |
| Gyehadze | Dam | 7.27 | 28.7 | 645.93 | 361.8 | 0.533 | 12.40 | 18.40 | 7.78 | 105.0 | 3.50 | 184.0 | 6.85 | 15.13 | 18.00 | 0.91 | 2.7 |
| Adawukwa | River | 7.74 | 27.05 | 347.95 | 221.7 | 0.220 | 18.93 | 8.00 | 19.80 | 33.00 | 3.70 | 84.5 | 34.54 | 23.10 | 0.109 | 0.67 | 1.1 |
| Adawukwa | River | 8.10 | 26.1 | 514.8 | 283.15 | 0.396 | 26.45 | 66.0 | 8.25 | 21.00 | 9.80 | 104.0 | 49.6 | 32.27 | 0.134 | 0.36 | 6.7 |
| Dominase | HDW | 8.10 | 26.5 | 1335.7 | 732.77 | 0.761 | 33.40 | 64.2 | 42.1 | 96.0 | 9.50 | 210.34 | 135.0 | 40.75 | 0.253 | 7.27 | 7.2 |
| A. Kwabenya | BH1 | 6.73 | 23.3 | 1844.5 | 799.4 | 0.830 | 16.80 | 69.7 | 34.5 | 64.0 | 7.50 | 254.2 | 28.02 | 20.50 | 4.00 | <0.001 | 6.8 |
| A.Kwabenya | BH2 | 6.71 | 22.4 | 1384.0 | 743.15 | 0.778 | 16.80 | 55.35 | 19.44 | 43.33 | 8.20 | 179.63 | 42.79 | 20.50 | 4.60 | 0.61 | 0.8 |
| A.Kwabenya | Stream | 7.35 | 21.1 | 832.7 | 517.5 | 0.512 | 16.80 | 53.0 | 20.05 | 29.6 | 1.50 | 181.94 | 12.1 | 20.50 | 0.058 | 0.06 | -0.6 |
| Ofaso | BH | 6.79 | 22.3 | 1494.0 | 744.6 | 0.776 | 22.90 | 48.36 | 39.85 | 65.92 | 6.00 | 205.0 | 87.586 | 27.94 | 3.663 | <0.001 | 3.8 |
| Dankwa | BH | 5.91 | 22.8 | 859.3 | 421.6 | 0.423 | 12.50 | 37.34 | 6.08 | 52.0 | 19.80 | 122.71 | 42.6 | 15.25 | 4.80 | 0.18 | 4.7 |
| Fianko | BH | 5.76 | 23.2 | 1286.5 | 633.9 | 0.656 | 8.40 | 50.58 | 32.7 | 85.0 | 23.00 | 239.81 | 53.47 | 10.25 | 0.141 | <0.001 | 8.5 |
| Penin | BH1 | 6.49 | 24.9 | 1.805.5 | 891.7 | 0.941 | 28.40 | 52.16 | 39.63 | 99.0 | 60.50 | 287.93 | 119.42 | 34.65 | 0.141 | 0.12 | 2.6 |
| Penin | BH2 | 6.14 | 24.7 | 982.95 | 496.4 | 0.504 | 18.40 | 63.33 | 37.86 | 78.0 | 8.70 | 191.98 | 142.0 | 22.45 | 0.141 | 0.31 | 6.4 |
| Penin | Stream | 6.62 | 22.5 | 538.7 | 268.0 | 0.265 | 6.80 | 38.70 | 13.77 | 19.9 | 6.10 | 91.984 | 46.28 | 8.296 | 0.006 | 0.64 | 5 |

Appendix 3
continued

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Oismpo | BH | 6.46 | 27.5 | 1217.5 | 772.9 | 0.814 | 25.60 | 64.60 | 53.2 | 51.3 | 5.70 | 223.35 | 112.59 | 31.23 | 0.184 | 1.03 | 4.4 |
| Osimpo | Stream | 5.17 | 23.4 | 483.60 | 301.2 | 0.304 | 25.40 | 32.70 | 21.8 | 42.5 | 4.90 | 96.46 | 65.6 | 30.99 | 0.921 | 0.23 | 8.1 |
| Ayensuako | BH | 7.13 | 27.3 | 712.75 | 435.23 | 0.442 | 13.80 | 37.50 | 21.3 | 96.0 | 6.30 | 157.69 | 118.0 | 16.84 | 0.105 | 0.06 | 5.3 |
| Ag.Tekyeman | BH | 6.24 | 29.0 | 740.83 | 396.83 | 0.397 | 13.60 | 37.00 | 21.2 | 51.0 | 4.70 | 113.6 | 72.34 | 16.59 | 0.045 | <0.001 | 8.9 |
| Kwakwa | River | 7.96 | 27.4 | 234.53 | 131.17 | 0.125 | 7.20 | 39.41 | 5.265 | 18.0 | 2.70 | 84.0 | 48.030 | 8.78 | 2.287 | 0.08 | -4.2 |
| Mankrong | River | 7.86 | 27.95 | 217.07 | 117.87 | 0.113 | 5.60 | 23.21 | 4.83 | 8.5 | 1.70 | 46.29 | 20.68 | 6.83 | 1.20 | 2.22 | 1 |
| Obosomase | BH | 6.53 | 22.5 | 685.5 | 301.65 | 0.298 | 7.30 | 38.00 | 32.3 | 72.0 | 6.60 | 168.63 | 92.6 | 8.91 | 0.08 | 0.77 | 7.1 |
| Obosomase | Stream | 7.10 | 23.2 | 821.55 | 339.5 | 0.347 | 7.20 | 31.8 | 21.2 | 37.0 | 6.50 | 99.4 | 66.183 | 8.78 | 0.080 | 0.07 | 8.5 |
| Kokoado | BH | 6.04 | 24.4 | 1652.0 | 686.7 | 0.714 | 7.20 | 42.93 | 32.4 | 57.0 | 23.95 | 114.29 | 171.0 | 8.78 | 0.114 | 0.82 | 6.6 |
| Mensakwa | BH | 6.20 | 23.3 | 1463.0 | 602.95 | 0.618 | 7.00 | 28.79 | 23.85 | 91.0 | 6.70 | 185.55 | 87.2 | 8.54 | 0.153 | <0.001 | 2.5 |
| Esselkwa | BH | 6.02 | 24.4 | 1204.0 | 520.8 | 0.540 | 6.60 | 40.00 | 31.5 | 61.0 | 9.20 | 127.1 | 137.0 | 8.05 | 0.031 | 8.38 | 4.8 |
| Amanfor | BH1 | 5.58 | 23.9 | 841.65 | 347.95 | 0.350 | 7.20 | 21.20 | 41.34 | 101.0 | 7.20 | 158.8 | 153.0 | 8.78 | 0.098 | 0.27 | 7.5 |
| Amanfor | BH2 | 6.03 | 28.2 | 987.1 | 389.9 | 0.388 | 9.60 | 21.20 | 35.00 | 71.5 | 7.80 | 163.9 | 121.9 | 11.71 | 0.306 | 1.15 | -0.7 |
| Namonwura | BH1 | 5.19 | 26.3 | 504.75 | 208.7 | 0.205 | 9.60 | 35.00 | 15.00 | 37.0 | 2.90 | 98.7 | 68.0 | 11.71 | 0.125 | <0.001 | 3.2 |
| Namonwura | BH2 | 5.89 | 27.8 | 256.4 | 101.7 | 0.096 | 8.00 | 31.40 | 21.89 | 43.0 | 4.80 | 94.7 | 82.88 | 9.76 | 0.183 | 17.7 | 2.6 |
| Ohiawanwu | BH | 5.37 | 26.3 | 603.9 | 249.05 | 0.245 | 5.47 | 21.20 | 9.75 | 70.0 | 11.00 | 131.63 | 83.99 | 6.67 | 0.137 | 1.32 | -3.8 |
| Otabilkwa | BH | 5.28 | 25.7 | 721.35 | 297.3 | 0.298 | 5.00 | 33.33 | 22.5 | 63.0 | 14.00 | 102.3 | 81.6 | 6.10 | 15.88 | <0.001 | 15 |
| Kwesikukwa | BH | 4.77 | 25.3 | 336.2 | 143.0 | 0.139 | 5.60 | 21.20 | 27.4 | 25.8 | 9.00 | 53.25 | 115.48 | 6.83 | 0.161 | <0.001 | 7.7 |
| Doato | BH1 | 5.42 | 24.0 | 562.55 | 229.4 | 0.227 | 5.00 | 37.15 | 31.3 | 57.0 | 10.30 | 182.29 | 42.0 | 6.10 | 0.051 | 2.35 | 7.6 |
| Doato | BH2 | 5.73 | 22.8 | 708.6 | 305.5 | 0.308 | 5.60 | 32.33 | 21.23 | 21.0 | 9.10 | 99.8 | 64.5 | 6.83 | 0.051 | <0.001 | 3 |
| Kanyanko | BH1 | 5.92 | 24.3 | 839.6 | 420.6 | 0.426 | 6.40 | 31.80 | 10.6 | 49.0 | 22.00 | 96.31 | 78.9 | 7.81 | 6.34 | <0.001 | 6 |
| Kanyanko | BH2 | 5.98 | 24.5 | 850.55 | 275.1 | 0.253 | 4.00 | 40.00 | 10.60 | 65.5 | 11.90 | 118.89 | 96.3 | 4.88 | 0.074 | <0.001 | 5.2 |
| F.Bawjoase | BH1 | 6.20 | 24.5 | 1106.0 | 455.1 | 0.461 | 5.00 | 39.73 | 5.30 | 98.0 | 11.50 | 182.29 | 62.2 | 6.10 | 0.07 | <0.001 | 3.3 |
| F.Bawjoase | BH2 | 5.75 | 24.7 | 875.35 | 360.15 | 0.364 | 5.60 | 35.37 | 31.80 | 89.5 | 8.30 | 225.74 | 64.8 | 6.83 | 0.091 | <0.001 | 4.3 |

*Appendix 3*
*continued*

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Kofikumkwa | BH | 6.05 | 28.5 | 542.05 | 266.95 | 0.263 | 6.00 | 42.30 | 32.4 | 43.0 | 7.70 | 124.09 | 104.0 | 7.32 | 0.032 | <0.001 | 8.7 |
| Oboyambo | HDW1 | 6.81 | 28.0 | 1340.5 | 665.8 | 0.689 | 11.20 | 42.00 | 35.40 | 123.9 | 16.10 | 168.7 | 209.0 | 13.66 | 0.206 | <0.001 | 7.5 |
| Oboyambo | BH | 6.24 | 25.8 | 856.1 | 344.4 | 0.341 | 11.40 | 43.40 | 25.45 | 61.0 | 4.20 | 139.0 | 97.8 | 13.91 | 0.635 | <0.001 | 6.5 |
| Oboyambo | HDW2 | 5.98 | 27.8 | 297.65 | 137.1 | 0.133 | 4.53 | 31.00 | 5.30 | 76.4 | 10.60 | 118.8 | 90.8 | 5.53 | 0.203 | 0.41 | 2.2 |
| Oboyambo | HDW3 | 7.06 | 28.2 | 464.6 | 184.6 | 0.179 | 1.20 | 21.20 | 26.50 | 33.15 | 4.30 | 87.0 | 98.5 | 1.46 | 0.056 | 0.25 | 3 |
| Okaekrom | BH | 5.75 | 27.7 | 821.55 | 402.5 | 0.403 | 7.13 | 42.40 | 21.80 | 118.0 | 6.80 | 206.96 | 98.4 | 8.70 | 0.184 | <0.001 | 7 |
| Bewadze | BH | 6.67 | 29.3 | 1380.5 | 896.7 | 0.933 | 14.87 | 31.80 | 46.7 | 153.7 | 15.30 | 303.53 | 82.5 | 18.14 | 0.139 | <0.001 | 8.6 |
| Aduafokwa | BH | 7.65 | 28.3 | 1736.0 | 1084.0 | 1.165 | 10.65 | 46.30 | 48.0 | 182.6 | 73.00 | 362.1 | 176.3 | 12.99 | 0.139 | <0.001 | 6.7 |
| Alabra | BH | 7.10 | 26.85 | 960.1 | 620.68 | 0.632 | 9.97 | 55.65 | 10.6 | 116.0 | 2.00 | 184.63 | 164.0 | 12.16 | 0.191 | 0.10 | -0.4 |
| Asabrekwa | River | 7.54 | 27.6 | 635.6 | 238.8 | 0.231 | 12.60 | 31.80 | 21.2 | 66.0 | 10.80 | 139.0 | 65..9 | 15.37 | 0.088 | 0.23 | 7.9 |
| Kyerebuakwa | BH | 6.36 | 28.1 | 678.7 | 269.7 | 0.266 | 16.00 | 42.54 | 32.6 | 41.0 | 6.40 | 117.36 | 94.6 | 19.52 | 0.145 | <0.001 | 9.6 |
| Kokroko | BH | 5.99 | 28.1 | 1012.6 | 400.1 | 0.400 | 16.00 | 8.75 | 43.46 | 109.0 | 8.60 | 243.18 | 43.46 | 19.52 | 0.146 | 5.23 | 4.5 |
| Kokroabo | BH | 6.20 | 28.0 | 515.3 | 204.8 | 0.200 | 18.60 | 40.10 | 24.80 | 51.0 | 5.70 | 113.75 | 80.5 | 22.69 | 0.132 | 5.10 | 8.6 |
| Brahabekume | BH | 6.69 | 27.2 | 7711.0 | 3062.0 | 3.319 | 19.40 | 625.00 | 122.0 | 338.0 | 5.40 | 1524.0 | 406.0 | 23.67 | 0.145 | <0.001 | 4.1 |
| Topiase | BH | 6.12 | 27.0 | 3347.0 | 1331.0 | 1.409 | 12.96 | 96.50 | 46.50 | 125.5 | 8.90 | 248.0 | 333.00 | 15.81 | 0.058 | <0.001 | 0.7 |

## Appendix 4. Saturation indices for carbonate, iron bearing mineral gypsum, albite, anhydrite, amorphous silicate and quart.

| No. | SAMPLE ID | TYPE | TEMP | pH | Si_Cal | Si_Dol | Si_Gyp | Si_Goe | Si_Sid | Si_Quarz | Si_SiO2(a) | Si_Fe(OH)3 | Si_Alb | Si_Hal | Si_Anh | Si_He |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Alabra | BH | 26.9 | 7.10 | -256 | -512 | -1.53 | 8.39 | -264.6 | 0.94 | -0.29 | 2.43 | 2.53 | -6.27 | -1.74 | 18.7 |
| 2 | Amanfor | BH1 | 23.90 | 5.58 | -3.74 | -6.86 | -2.00 | 7.02 | -10.58 | 1.08 | -0.18 | 1.17 | 0.21 | -6.40 | -2.23 | 16.05 |
| 3 | Amanfor | BH2 | 28.20 | 6.03 | -4.73 | -8.86 | -2.07 | 7.51 | -11.89 | 1.01 | -0.21 | 1.51 | 1.75 | -6.54 | -2.28 | 17.05 |
| 4 | Ayensuako | BH | 27.30 | 7.13 | -251 | -502 | -1.83 | 8.20 | -259.9 | 0.92 | -0.31 | 2.23 | 2.20 | -6.43 | -2.04 | 18.42 |
| 5 | Doato | BH1 | 24.00 | 5.42 | -258.2 | -516.2 | -2.13 | 7.13 | -264.8 | 0.91 | -0.34 | 1.32 | 0.23 | -6.44 | -2.35 | 16.35 |
| 6 | Doato | BH2 | 22.80 | 5.73 | -257 | -514 | -1.91 | 7.45 | -264.1 | 1.05 | -0.21 | 1.64 | 0.72 | -7.25 | -2.14 | 16.91 |
| 7 | Dominase | HDW | 26.50 | 8.10 | -0.29 | -0.39 | -1.63 | 8.47 | -11.13 | 0.99 | -0.24 | 2.52 | 2.38 | -6.31 | -1.84 | 18.95 |
| 8 | Esselkwa | BH | 24.40 | 6.02 | -258 | -516 | -1.48 | 7.97 | -265.7 | 1.04 | -0.21 | 2.1 | 2.09 | -6.75 | -1.71 | 17.95 |
| 9 | F. Bawjiase | BH1 | 24.50 | 6.20 | -259 | -517 | -1.13 | 8.53 | -266.1 | 1.12 | -0.13 | 2.66 | 2.53 | -6.4 | -1.36 | 19.06 |
| 10 | F. Bawjiase | BH2 | 24.70 | 5.75 | -258 | -515 | -1.83 | 7.60 | -264.7 | 1.12 | -0.13 | 1.72 | 1.69 | -6.28 | -2.05 | 17.21 |
| 11 | Gyangyan. | BH | 27.7 | 7.73 | -0.62 | -1.55 | -1.32 | 8.72 | -9.79 | 0.86 | -0.36 | 2.70 | 1.86 | -5.32 | -1.52 | 19.47 |
| 12 | Kanyanko | BH2 | 24.50 | 5.98 | -3.22 | -6.68 | -1.84 | 5.59 | -12.6 | 0.99 | -0.26 | -0.28 | -1.31 | -6.7 | -2.06 | 13.18 |
| 13 | Kofikum | BH | 28.50 | 6.05 | -256 | -513 | -1.46 | 7.97 | -263.7 | 0.99 | -0.23 | 1.95 | 1.43 | -6.87 | -1.67 | 17.96 |
| 14 | Kokoado | BH | 24.40 | 6.04 | -256 | -512 | -1.30 | 7.78 | -264 | 1.19 | -0.06 | 1.91 | 2.21 | -6.78 | -1.52 | 17.37 |
| 15 | KoKroabo | BH | 28.00 | 6.20 | -2.56 | -5.01 | -1.94 | 8.52 | -9.39 | 0.96 | -0.26 | 2.53 | 1.60 | -6.84 | -2.15 | 19.07 |
| 16 | Kokroko | BH | 28.10 | 5.99 | -4.18 | -7.23 | -2.90 | 7.66 | -10.76 | 0.51 | -0.71 | 1.66 | 0.58 | -6.19 | -3.11 | 17.34 |
| 17 | Kweikrom | HDW | 30.40 | 6.79 | -1.51 | -3.28 | -1.81 | 6.17 | -11.99 | 0.82 | -0.41 | 0.21 | 0.92 | -6.39 | -2.02 | 14.36 |
| 18 | Kwesikukw | BH | 25.30 | 4.77 | -4.57 | -8.69 | -2.05 | 6.43 | -10.4 | 0.93 | -0.32 | 0.53 | -2.40 | -7.45 | -2.27 | 14.86 |
| 19 | Mensakwa | BH | 23.30 | 6.20 | -2.64 | -5.56 | -1.79 | 5.17 | -11.75 | 0.93 | -0.30 | -0.79 | -1.42 | -6.34 | -2.00 | 12.36 |
| 20 | Namonwura | BH2 | 27.80 | 5.89 | -3.12 | -6.03 | -2.01 | 5.00 | -12.73 | 1.02 | -0.21 | -0.99 | 0.46 | -6.99 | -2.22 | 12.03 |
| 21 | Oboyambo | HD1 | 28.00 | 6.81 | -255 | -511 | -1.60 | 8.47 | -263.4 | 0.95 | -0.27 | 2.57 | 2.51 | -6.31 | -1.82 | 18.96 |
| 22 | Oboyambo | HD2 | 27.80 | 5.89 | -257 | -514 | -1.50 | 8.12 | -264.4 | 0.79 | -0.44 | 2.13 | 0.9 | -6.63 | -1.71 | 18.25 |

Appendix 4 continued

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 23 | Oboyambo | HD3 | 28.20 | 7.06 | -263 | -526 | -2.32 | 8.24 | -270.8 | 0.90 | -0.32 | 2.24 | 1.86 | -7.08 | -2.52 | 18. |
| 24 | Obosomase | BH | 22.50 | 6.53 | -258 | -516 | -1.84 | 8.00 | -266 | 1.01 | -0.25 | 2.20 | 2.36 | -6.51 | -2.07 | 17.9 |
| 25 | Ohiawonwu | BH | 26.30 | 5.37 | -3.97 | -7.93 | -2.15 | 4.70 | -12.71 | 0.91 | -0.32 | -1.24 | -0.84 | -6.63 | -2.36 | 11.4 |
| 26 | Ojobi | BH | 25.2 | 7.16 | -253 | -505.3 | -2.03 | 8.30 | -261.8 | 0.27 | -0.97 | 2.4 | 0.85 | -5.46 | -2.25 | 18.61 |

Appendix 5: Trace metal concentrations of water samples in the Ayensu River Basin during the dry season.

| No. | Location | Type | Fe | Cu | Zn | Cr | Cd | Mn | Al |
|---|---|---|---|---|---|---|---|---|---|
| 1. | Ojobi | BH | 1.20 | <0.003 | 0.006 | <0.001 | <0.002 | 0.101 | 0.32 |
| 2. | Ojobi | HDW | 0.44 | <0.003 | 0.091 | <0.006 | 0.058 | 0.035 | 0.03 |
| 3. | Ojobi | Pond | 0.524 | <0.003 | 0.141 | <0.006 | 0.082 | 0.16 | 0.030 |
| 4. | Ojobi | Spring | 1.55 | <0.003 | 0.056 | <0.006 | 0.079 | 0.03 | <0.030 |
| 5. | Kweikrom | BH | <0.006 | 0.054 | 0.018 | <0.006 | <0.00 | <0.002 | 0.258 |
| 6. | Kweikrom | HDW1 | <0.006 | <0.003 | 0.007 | <0.006 | <0.002 | <0.002 | 0.32 |
| 7. | Kweikrom | HDW2 | <0.006 | <0.003 | 0.017 | <0.006 | <0.002 | 0.011 | 0.24 |
| 8. | Gyangyanadze | BH | 1.465 | <0.003 | 0.027 | 0.003 | <0.002 | 0.002 | 0.438 |
| 9. | Gyehadze | Dam | 1.67 | 0.016 | 0.301 | <0.006 | <0.002 | 0.002 | <0.03 |
| 10 | Adawukwa | River1 | 0.989 | <0.003 | 0.073 | <0.006 | 0.081 | 0.016 | 0.107 |
| 11. | Adawukwa | River2 | 0.01 | <0.003 | 0.048 | <0.006 | <0.002 | 0.35 | <0.030 |
| 12. | Dominase | HDW | 0.48 | <0.003 | 0.06 | <0.006 | 0.073 | <0.002 | <0.03 |
| 13. | Awutu Kwabenya | BH1 | 0.038 | <0.003 | 0.018 | <0.006 | <0.002 | 0.04 | 0.21 |
| 14. | Awutu Kwabenya | BH2 | 0.044 | 0.003 | 0.128 | <0.006 | <0.002 | 0.034 | <0.03 |
| 15. | Awutu Kwabenya | St. | 0.311 | <0.003 | 0.086 | <0.006 | 0.081 | 0.048 | <0.03 |
| 16. | Ofaso | BH | 0.177 | <0.006 | 0.06 | <0.006 | <0.002 | <0.002 | 0.03 |
| 17. | Dankwa | BH | 0.045 | <0.006 | 0.072 | <0.006 | <0.002 | 0.003 | <0.03 |
| 18. | Fianko | BH | 0.01 | <0.006 | 0.065 | <0.006 | <0.002 | <0.002 | 0.003 |
| 19. | Penin | BH 1 | 0.027 | <0.006 | 0.05 | <0.006 | <0.002 | <0.002 | 0.003 |
| 20. | Penin | BH 2 | 0.116 | <0.006 | 0.002 | 0.005 | <0.002 | <0.002 | 0.354 |
| 21. | Penin | Str. | 0.876 | <0.006 | 0.057 | <0.006 | 0.081 | 0.034 | 0.030 |
| 22. | Osimpo | BH | 0.009 | <0.006 | 0.035 | <0.006 | <0.002 | <0.002 | 0.26 |
| 23. | Osimpo | Str. | 0.605 | <0.006 | 0.125 | <0.006 | 0.078 | 0.170 | 0.101 |
| 24. | Ayensuako | BH | 0.233 | 0.353 | 0.050 | <0.006 | 0.065 | <0.002 | 0.030 |
| 25. | Agona Tekyeman | BH | 4.245 | <0.006 | 0.072 | <0.006 | 0.002 | <0.002 | <0.03 |
| 26. | Kwakwa | River | 1.385 | <0.006 | 0.101 | <0.006 | 0.047 | 0.149 | <0.030 |
| 27. | Mankrong | Nkw. R. | 1.243 | <0.006 | 0.062 | <0.006 | 0.074 | 0.240 | 0.073 |
| 28. | Obosomase | BH | 0.006 | <0.006 | 0.194 | <0.006 | <0.002 | 0.008 | <0.03 |
| 29. | Obosomase | Str. | 0.049 | 0.010 | 0.092 | <0.006 | <0.002 | 0.027 | <0.03 |
| 30. | Kokoado | BH | <0.006 | <0.006 | 0.098 | <0.006 | <0.002 | 0.043 | 0.321 |
| 31. | Mensakwa | BH | <0.006 | 0.004 | 0.101 | <0.006 | <0002 | 0.276 | <0.03 |
| 32. | Esselkwa | BH | <0.006 | <0.006 | 0.146 | <0.006 | <0.002 | 0.06 | <0.03 |
| 33. | Amanfor | BH 1 | <0.006 | 0.006 | 0.172 | <0.006 | <0.002 | 0.016 | <0.03 |
| 34. | Amanfor | BH 2 | <0.006 | <0.006 | 0.012 | <0.006 | <0.002 | 0.011 | 0.30 |
| 35. | Namonwura | BH 1 | <0.006 | <0.003 | 0.332 | <0.006 | <0.002 | 0.10 | <0.003 |
| 36. | Namonwura | BH 2 | <0.006 | <0.003 | 0.361 | <0.006 | <0.002 | <0.002 | 0.28 |
| 37. | Ohiawonwu | BH | <0.006 | <0.003 | 0.067 | <0.006 | <0.002 | 0.39 | 0.31 |
| 38. | Otabilkwa | BH | <0.006 | <0.003 | 0.086 | <0.006 | <0.002 | 0.009 | <0.03 |
| 39. | Doato | BH 1 | <0.006 | <0.003 | 0.151 | <0.006 | <0.002 | <0.002 | 0.36 |
| 40. | Doato | BH 2 | <0.006 | 0.028 | 0.009 | 0.008 | <0.002 | 0.002 | <0.03 |
| 41. | Kanyanko | BH 1 | <0.006 | <0.003 | 0.180 | <0.006 | <0.002 | <0.002 | <0.03 |

Appendix 5 continued

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 42. | Kanyanko | BH 2 | <0.006 | 0.015 | 0.388 | <0.006 | <0.002 | 0.002 | <0.03 |
| 43. | Fante Bajwase | BH 1 | <0.006 | <0.003 | 0.116 | <0.006 | <0.002 | 0.012 | <0.03 |
| 44. | Fante Bajwase | BH 2 | <0.006 | <0.003 | 0.107 | <0.006 | <0.002 | 0.011 | <0.03 |
| 45. | Kofikum | BH | <0.006 | <0.003 | 0.150 | <0.006 | <0.002 | <0.002 | 0.05 |
| 46. | Oboyambo | HDW1 | <0.006 | <0.003 | 0.032 | <0.006 | <0.002 | 0.027 | 0.25 |
| 47. | Oboyambo | BH | <0.006 | 0.086 | 0.113 | <0.006 | <0.002 | 0.046 | <0.03 |
| 48. | Oboyambo | HDW2 | <0.006 | <0.003 | 0.058 | <0.006 | <0.002 | <0.002 | 0.31 |
| 49. | Oboyambo | HDW3 | <0.006 | <0.003 | 0.056 | <0.006 | <0.002 | <0.002 | 0.26 |
| 50. | Okaekrom | BH | 0.099 | <0.003 | 0.260 | <0.006 | <0.002 | 0.065 | <0.03 |
| 51. | Bewadze | BH | 0.046 | <0.003 | 0.019 | <0.006 | <0.002 | 0.002 | <0.03 |
| 52. | Alabra | BH | 0.219 | <0.003 | 0.046 | <0.006 | <0.002 | 0.002 | <0.03 |
| 53. | Asabrekwa | R.Ob | 0.034 | <0.003 | 0.129 | <0.006 | <0.002 | <0.002 | 0.20 |
| 54. | Kyerebuakwa | BH | <0.006 | <0.003 | 0.021 | <0.006 | <0.002 | <0.002 | 0.31 |
| 55. | Kokroko | BH | <0.006 | <0.003 | 0.020 | <0.006 | <0.002 | 0.041 | 0.23 |
| 56. | Kokroabo | BH | 0.018 | <0.003 | 0.035 | 0.009 | <0.002 | <0.002 | 0.272 |
| 57. | Brahabekume | BH | <0.006 | 0.006 | 0.126 | <0.006 | <0.002 | 0.037 | 0.266 |
| 58. | Topiase | BH | <0.006 | 0.005 | 0.142 | <0.006 | <0.002 | 0.010 | 0.279 |

**Appendix 6: Trace metal concentrations of water samples in the Ayensu River Basin during the rainy season.**

| No. | Location | Type | Cu | Zn | Mn | Al | Cd | Cr | Fe |
|---|---|---|---|---|---|---|---|---|---|
| 1. | Ojobi | BH | 1.100 | 0.200 | 0.101 | 2.324 | <0.002 | 0.192 | 0.516 |
| 2. | Ojobi | HDW | 0.86 | 0.254 | 0.035 | 3.58 | 0.016 | 0.172 | 1.258 |
| 3. | Ojobi | Pond | 0.288 | 0.025 | 0.561 | 0.035 | 0.082 | 0.363 | 0.524 |
| 4 | .Ojobi | Spring | 0.150 | 0.129 | 0.132 | <0.030 | 0.079 | 1.010 | 1.554 |
| 5. | Kweikrom | BH | 0.054 | 0.027 | <0.002 | 0.315 | <0.002 | <0.006 | <0.006 |
| 6. | Kweikrom | HDW2 | 0.964 | 0.176 | 0.011 | 3.124 | 0.016 | 0.280 | 0.860 |
| 7. | Gyangyanadze | BH | <0.003 | 0.042 | 0.006 | 0.438 | <0.002 | <0.006 | 1.465 |
| 9 | Adawukwa | River 1 | <0.003 | 0.073 | 0.055 | 0.107 | 0.081 | <0.006 | 0.989 |
| 10. | Adawukwa | River2 | <0.003 | 0.328 | 0.048 | <0.003 | 0.00 | 0.00 | 0.410 |
| 11. | Dominase | HDW1 | 0.096 | 0.184 | 0.006 | 1.724 | <0.002 | 0.040 | 0.604 |
| 12. | A.Kwabenya | BH 1 | <0.003 | 0.027 | 0.041 | 0.211 | <0.002 | <0.006 | 0.028 |
| 13. | A.Kwabenya | BH 2 | <0.003 | 0.159 | 0.034 | <0.030 | <0.002 | <0.006 | 0.045 |
| 14. | A.Kwabenya | Str. | <0.003 | 0.086 | 0.174 | <0.030 | 0.081 | <0.006 | 0.311 |
| 15. | Ofaso | BH | <0.003 | 0.091 | <0.002 | <0.030 | <0.002 | <0.006 | 0.117 |
| 16. | Dankwa | BH | 0.016 | 0.465 | 0.003 | <0.030 | <0.002 | <0.006 | 0.045 |
| 17. | Fianko | BH | <0.003 | 0.101 | 0.030 | <0.030 | <0.002 | <0.006 | <0.006 |
| 18. | Penin | BH 1 | 0.864 | 0.204 | 0.00 | 2.832 | 0.016 | 0.144 | 0.764 |
| 19. | Penin | Str. | <0.003 | 0.057 | 0.140 | <0.030 | 0.081 | <0.006 | 0.876 |
| 20. | Osimpo | BH | 0.824 | 0.128 | <0.002 | 2.692 | <0.002 | 0.124 | 0.632 |
| 21. | Osimpo | Str. | <0.003 | 0.125 | 0.551 | 0.101 | 0.078 | <0.006 | 0.605 |
| 22. | Ayensuako | BH | 0.996 | 0.136 | 0.004 | 2.008 | <0.002 | <0.006 | 0.452 |
| 23. | Ag.Tekyeman | BH | <0.003 | 0.054 | 0.016 | <0.030 | <0.002 | <0.006 | 0.009 |
| 24. | Kwakwa | River | 0.020 | 0.101 | 0.149 | 0.047 | <0.002 | <0.006 | 1.385 |
| 25. | M. Nkwanta | River | <0.003 | 0.062 | 0.108 | 0.073 | 0.074 | <0.006 | 1.243 |
| 26. | Obosomase | BH | 1.024 | 0.196 | 0.008 | 2.488 | <0.002 | 0.148 | 0.512 |
| 27. | Obosomase | Str. | 0.020 | 0.038 | 0.062 | <0.030 | <0.002 | <0.006 | 0.801 |
| 28. | Kokoado | BH | 0.944 | 0.116 | 0.043 | 2.372 | <0.002 | 0.252 | 0.540 |
| 29. | Mensakwa | BH | 0.010 | 0.092 | 0.276 | <0.030 | <0.002 | <0.006 | 0.049 |
| 30. | Esselkwa | BH | 1.028 | 0.140 | 0.060 | 2.988 | <0.002 | 0.068 | 0.156 |
| 31. | Ksikumkwa | BH | 0.924 | 0.136 | <0.002 | 2.704 | <0.002 | 0.244 | 0.652 |
| 32. | Amanfor | BH 2 | 1.108 | 0.164 | 0.011 | 2.044 | <0.002 | <0.006 | 0.492 |
| 33. | Namonwura | BH 1 | 0.004 | 0.101 | 0.101 | <0.030 | <0.002 | <0.006 | <0.006 |
| 34. | Namonwura | BH 2 | <0.003 | 0.146 | <0.002 | 0.279 | <0.002 | <0.006 | <0.006 |
| 35. | Ohiawonwu | BH | 0.006 | 0.172 | 0.391 | 0.308 | <0.002 | <0.006 | <0.006 |
| 36. | Otabilkwa | BH | <0.003 | 0.332 | 0.009 | <0.030 | <0.002 | <0.006 | <0.006 |
| 37. | Doato | BH 1 | 1.040 | 0.312 | <0.002 | 3.036 | 0.024 | 0.180 | 0.684 |
| 38. | Doato | BH 2 | 0.916 | 0.128 | <0.002 | 2.276 | <0.00 | <0.006 | 0.560 |
| 39. | Kanyanko | BH 2 | 0.028 | 0.151 | <0.002 | <0.03 | <0.002 | <0.006 | <0.006 |
| 40. | Fante Bajwase | BH 1 | 1.000 | 0.180 | 0.012 | 3.160 | 0.028 | 0.112 | 0.820 |
| 41. | Fante Bajwase | BH 2 | 1.000 | 0.156 | 0.011 | 2.268 | <0.002 | 0.252 | 0.768 |
| 42. | Kofikum | BH | 1.084 | 0.200 | <0.002 | 1.692 | 0.008 | 0.364 | 0.534 |
| 43. | Oboyambo | HDW1 | 0.888 | 0.236 | 0.027 | 2.920 | 0.020 | 0.092 | 1.236 |

Appendix 6 continued

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 47. | Oboyambo | BH | <0.003 | 0.107 | 0.046 | <0.030 | <0.006 | | |
| 48. | Oboyambo | HDW2 | 1.044 | 0.204 | <0.002 | 1.440 | 0.012 | 0.248 | 0.852 |
| 49. | Oboyambo | HDW3 | 1.048 | 0.160 | <0.002 | 2.648 | <0.002 | 0.256 | 0.736 |
| 50. | Okaekrom | BH | 0.960 | 0.196 | 0.065 | 2.864 | <0.002 | 0.224 | 0.680 |
| 51. | Bewadze | BH | <0.003 | 0.067 | <0.002 | <0.030 | <0.002 | <0.006 | <0.006 |
| 52. | Alabra | BH | 1.000 | 0.178 | 0.163 | 2.970 | <0.002 | 0.216 | 0.710 |
| 53. | Asabrekwa | R. Oboyambo | 0.020 | 0.026 | 0.018 | 0.279 | <0.006 | 0.202 | |
| 54. | Kyerebuakwa | BH | <0.003 | 0.260 | 0.037 | 0.366 | <0.002 | <0.006 | 0.099 |
| 55. | Kokroko | BH | 0.880 | 0.176 | <0.002 | 3.188 | <0.002 | 0.136 | 0.752 |
| 56. | Kokroab0 | BH | 1.112 | 0.204 | <0.002 | 1.652 | <0.002 | 0.072 | 0.656 |
| 57. | Brahabekume | BH | 0.005 | 0.142 | 0.041 | 0.230 | <0.002 | <0.006 | <0.006 |
| 58. | Topiase | BH | 0.006 | 0.126 | <0.002 | 0.272 | <0.002 | <0.006 | <0.006 |

**Appendix 7: Stable isotope raw data for rainwater in the Ayensu river basin.**

| Sample No. | Sample Name | $\delta^2H$ Reportable Value (permil) | $\delta^2H$ Standard Deviation (permil) | $\delta^{18}O$ Reportable Value (permil) | $\delta^{18}O$ Standard Deviation (permil) | Analysis Date | $\delta^2H$ Quality (stdev <2) | $\delta^{18}O$ Quality (stdev <0.3) |
|---|---|---|---|---|---|---|---|---|
| 1 | Kwanyako Feb | -0.93 | 0.12 | -0.53 | 0.05 | 17-05-2012 | OK | OK |
| 2 | Kwanyako Mar | 1.31 | 0.25 | -0.37 | 0.13 | 17-05-2012 | OK | OK |
| 3 | Kwanyako Apr | 4.18 | 0.74 | 0.67 | 0.09 | 17-05-2012 | OK | OK |
| 4 | Kwanyako May | -2.53 | 0.49 | -0.28 | 0.06 | 17-05-2012 | OK | OK |
| 5 | Kwanyako June | 6.06 | 1.54 | 1.75 | 0.15 | 17-05-2012 | OK | OK |
| 6 | Swedru March | 3.74 | 0.13 | -0.65 | 0.09 | 17-05-2012 | OK | OK |
| 7 | Swedru May | -6.23 | 0.43 | -2.29 | 0.16 | 17-05-2012 | OK | OK |
| 8 | Swedru June | -5.24 | 0.24 | -1.70 | 0.02 | 17-05-2012 | OK | OK |
| 9 | Winneba February | -3.19 | 0.80 | -2.64 | 0.13 | 17-05-2012 | OK | OK |
| 10 | Winneba March | -8.26 | 1.08 | -2.52 | 0.13 | 17-05-2012 | OK | OK |
| 11 | Winneba May | -0.65 | 1.26 | -1.31 | 0.23 | 17-05-2012 | OK | OK |
| 12 | Winneba June | 4.48 | 0.72 | 0.70 | 0.07 | 17-05-2012 | OK | OK |
| 1 | KNKF | -1.72 | 0.97 | -0.18 | 0.05 | 15-05-2012 | OK | OK |
| 2 | KNKM | 0.87 | 0.01 | -0.28 | 0.05 | 15-05-2012 | OK | OK |
| 3 | KNKA | 3.69 | 0.55 | 0.73 | 0.15 | 15-05-2012 | OK | OK |
| 4 | KNKM | -1.91 | 0.53 | -0.35 | 0.07 | 15-05-2012 | OK | OK |
| 5 | KNKJ | 7.85 | 0.70 | 1.51 | 0.11 | 15-05-2012 | OK | OK |
| 6 | SWD M | 3.51 | 0.77 | -0.63 | 0.11 | 15-05-2012 | OK | OK |
| 7 | SWD M | -3.94 | 1.15 | -2.45 | 0.11 | 15-05-2012 | OK | OK |
| 8 | SWD J | -3.21 | 0.49 | -1.57 | 0.10 | 15-05-2012 | OK | OK |

|  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
| 9 | WNB F | -2.48 | 0.72 | -2.44 | 0.14 | 15-05-2012 | OK | OK |
| 10 | WNB M | -8.42 | 0.73 | -2.36 | 0.10 | 15-05-2012 | OK | OK |
| 11 | WNB M | 0.46 | 0.83 | -1.37 | 0.19 | 15-05-2012 | OK | OK |
| 12 | WNBJ | 4.78 | 0.65 | 0.43 | 0.12 | 15-05-2012 | OK | OK |
| 1 | Kwanyako February | 2.23 | 0.64 | -0.69 | 0.08 | 16-05-2012 | OK | OK |
| 2 | Kwanyako March | 2.94 | 1.19 | -0.59 | 0.03 | 16-05-2012 | OK | OK |
| 3 | Kwanyako April | 8.24 | 0.86 | 0.92 | 0.03 | 16-05-2012 | OK | OK |
| 4 | Kwanyako May | 1.36 | 0.24 | -0.24 | 0.08 | 16-05-2012 | OK | OK |
| 5 | Kwanyako June | 8.91 | 0.57 | 1.56 | 0.02 | 16-05-2012 | OK | OK |
| 6 | Swedru March | 0.22 | 0.05 | -0.72 | 0.07 | 16-05-2012 | OK | OK |
| 7 | Swedru May | -5.83 | 0.60 | -2.68 | 0.12 | 16-05-2012 | OK | OK |
| 8 | Swedru June | -2.85 | 0.39 | -1.83 | 0.09 | 16-05-2012 | OK | OK |
| 9 | Winneba February | -0.45 | 0.15 | -2.73 | 0.14 | 16-05-2012 | OK | OK |
| 10 | Winneba March | -4.67 | 0.05 | -2.63 | 0.26 | 16-05-2012 | OK | OK |
| 11 | Winneba May | -1.52 | 0.18 | -1.52 | 0.12 | 16-05-2012 | OK | OK |
| 12 | Winneba June | 2.66 | 0.83 | 0.36 | 0.02 | 16-05-2012 | OK | OK |

Apendix 8: Stable isotope data for groundwater and surfacewater (rivers and dams) in the Ayensu river basin.

| Sample No. | Sample Name | $\delta^2H$ Reportable Value (permil) | $\delta^2H$ Standard Deviation (permil) | $\delta^{18}O$ Reportable Value (permil) | $\delta^{18}O$ Standard Deviation (permil) | Analysis Date | $\delta^2H$ Quality (stdev <2) | $\delta^{18}O$ Quality (stdev <0.3) |
|---|---|---|---|---|---|---|---|---|
| 1 | KANYANKO BH | -7.81 | 1.14 | -2.06 | 0.13 | 31-05-2011 | OK | OK |
| 2 | OSIMPO BH | -4.65 | 0.20 | -1.54 | 0.14 | 31-05-2011 | OK | OK |
| 3 | AWUTU KWABENYA BH2 | -4.77 | 1.18 | -1.86 | 0.12 | 31-05-2011 | OK | OK |
| 4 | KOKROABO BH | -7.59 | 1.00 | -1.74 | 0.17 | 31-05-2011 | OK | OK |
| 5 | KWEIKROM BH | -8.77 | 1.06 | -2.21 | 0.12 | 31-05-2011 | OK | OK |
| 6 | KANYANKO | 0.59 | 0.63 | -0.85 | 0.15 | 31-05-2011 | OK | OK |
| 7 | AMANFOR BH2 | -8.21 | 1.04 | -2.34 | 0.16 | 31-05-2011 | OK | OK |
| 8 | OBOSOMASE BH | -6.95 | 1.37 | -2.31 | 0.14 | 31-05-2011 | OK | OK |
| 9 | OJOBI BH | -8.13 | 1.14 | -2.34 | 0.07 | 31-05-2011 | OK | OK |
| 10 | GYANGYANADZE BH | -14.22 | 0.54 | -3.12 | 0.10 | 31-05-2011 | OK | OK |
| 11 | PENIN BH2 | -6.87 | 0.54 | -3.00 | 0.10 | 31-05-2011 | OK | OK |
| 12 | MANKRONG R.AYENSU | -0.52 | 0.26 | -1.65 | 0.04 | 31-05-2011 | OK | OK |
| 13 | SWEDRU R.W | 11.69 | 0.26 | -0.09 | 0.13 | 31-05-2011 | OK | OK |
| 14 | DUATO BH2 | -6.63 | 0.40 | -2.35 | 0.07 | 31-05-2011 | OK | OK |
| 15 | OFASO BH | -8.26 | 1.45 | -2.46 | 0.16 | 31-05-2011 | OK | OK |
| 16 | FIANKO BH | -10.55 | 1.64 | -2.23 | 0.13 | 31-05-2011 | OK | OK |
| 17 | PENIN STREAM | -5.11 | 0.58 | -1.75 | 0.12 | 31-05-2011 | OK | OK |
| 18 | G. SAMPA 2 | -8.19 | 1.05 | -2.24 | 0.19 | 31-05-2011 | OK | OK |
| 19 | KOFIKUM BH | -6.68 | 0.57 | -2.43 | 0.06 | 31-05-2011 | OK | OK |

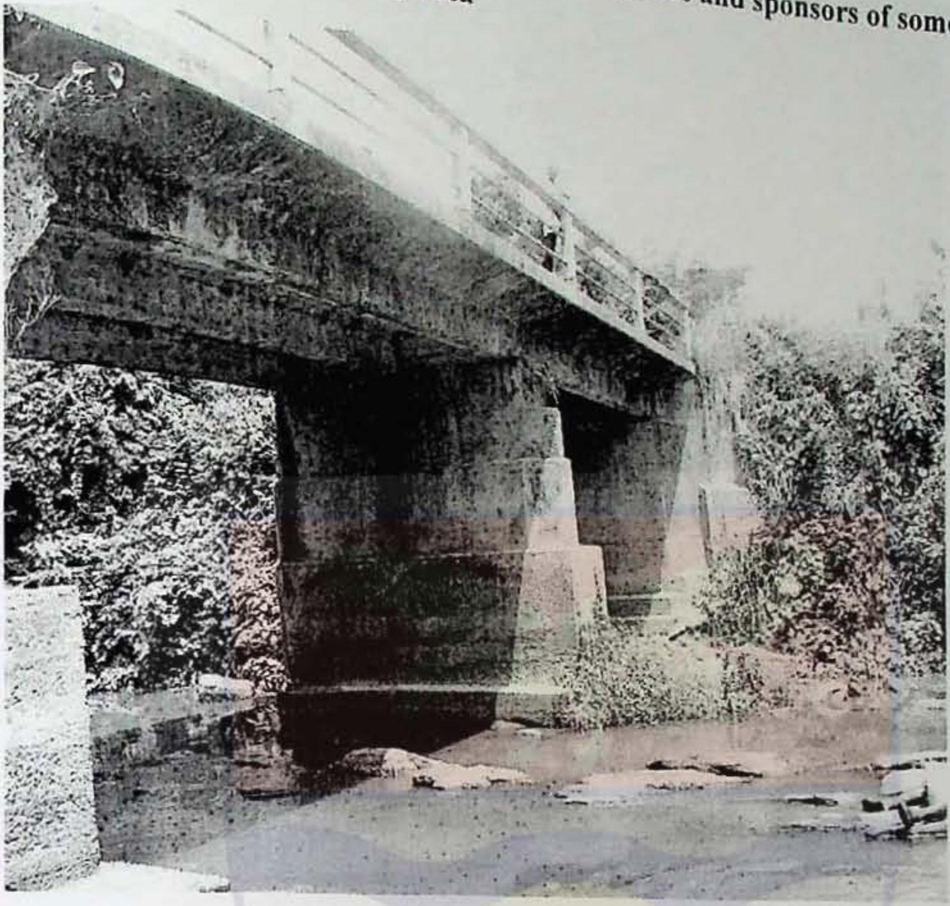
Appendix 8 continued

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 20 | NAMANWURA BH 1 | -6.02 | 0.76 | -2.26 | 0.23 | 31-05-2011 | OK | OK |
| 21 | A. KWABEYNA STR. | 0.83 | 0.72 | -1.31 | 0.16 | 31-05-2011 | OK | OK |
| 22 | OBOSOMASE STREAM | -0.45 | 1.71 | -0.83 | 0.24 | 31-05-2011 | OK | OK |
| 23 | OJOBI POND | -0.33 | 0.76 | -0.99 | 0.04 | 31-05-2011 | OK | OK |
| 24 | GYAHADZE DAM | 9.54 | 0.94 | 2.03 | 0.14 | 31-05-2011 | OK | OK |
| 25 | BIWADZE BH | -6.06 | 1.00 | -1.72 | 0.13 | 31-05-2011 | OK | OK |
| 26 | OSIMPO STREAM | -4.41 | 1.00 | -1.05 | 0.14 | 31-05-2011 | OK | OK |
| 27 | OBOYAMBO | -7.41 | 0.36 | -1.62 | 0.15 | 31-05-2011 | OK | OK |
| 28 | TOPIASE BH | -8.46 | 1.57 | -2.02 | 0.11 | 31-05-2011 | OK | OK |
| 29 | WINNEBA R.WATER | -7.53 | 0.94 | -1.81 | 0.09 | 31-05-2011 | OK | OK |
| 30 | AG. TEKYEMAN BH | -6.82 | 1.29 | -2.29 | 0.18 | 31-05-2011 | OK | OK |
| 1 | DANKWAA BH | -9.04 | 0.66 | -2.59 | 0.05 | 07-06-2011 | OK | OK |
| 2 | KWEIKROM | -7.75 | 0.41 | -2.61 | 0.13 | 07-06-2011 | OK | OK |
| 3 | OBOYOMBO BH | -7.29 | 0.37 | -2.58 | 0.12 | 07-06-2011 | OK | OK |
| 4 | DUATO BH1 | -7.71 | 0.89 | -2.31 | 0.07 | 07-06-2011 | OK | OK |
| 5 | ADABRA BH | -11.78 | 1.08 | -2.74 | 0.05 | 07-06-2011 | OK | OK |
| 6 | KANYAKO BH2 | -5.61 | 1.21 | -2.20 | 0.12 | 07-06-2011 | OK | OK |
| 7 | KOKOROKO BH | -7.99 | 0.86 | -2.84 | 0.20 | 07-06-2011 | OK | OK |
| 8 | OJOBI SPRING | -3.57 | 0.75 | -2.16 | 0.08 | 07-06-2011 | OK | OK |
| 9 | PENIN BH1 | -3.60 | 0.97 | -1.95 | 0.14 | 07-06-2011 | OK | OK |
| 10 | KWAKWA R.AYENSU | -1.54 | 0.63 | -1.62 | 0.15 | 07-06-2011 | OK | OK |
| 11 | NAMANWURA BH2 | -9.82 | 0.51 | -2.72 | 0.13 | 07-06-2011 | OK | OK |
| 12 | OBOYAMBO HDW2 | -6.18 | 0.47 | -2.13 | 0.12 | 07-06-2011 | OK | OK |
| 13 | MENSAKWAA BH | -8.00 | 0.63 | -2.36 | 0.05 | 07-06-2011 | OK | OK |
| 14 | AMANFOR BH1 | -8.72 | 0.66 | -2.50 | 0.11 | 07-06-2011 | OK | OK |

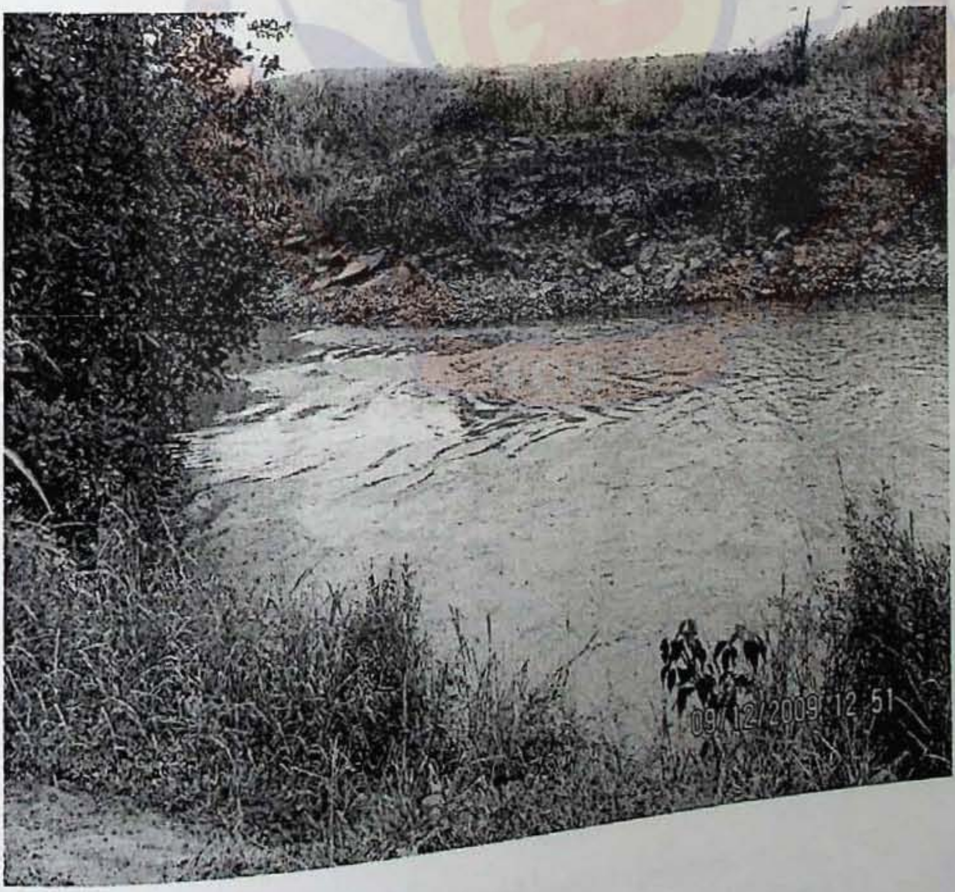
Appendix 8 continued

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 15 | BEWADZE BH | -7.15 | 0.34 | -1.91 | 0.14 | 07-06-2011 | OK | OK |
| 16 | A. KWABENYA BH1 | -9.11 | 0.64 | -2.28 | 0.18 | 07-06-2011 | OK | OK |
| 17 | AYENSUAKO BH | -4.29 | 0.77 | -1.42 | 0.19 | 07-06-2011 | OK | OK |
| 18 | KOKOADO BH | -7.61 | 0.86 | -2.53 | 0.17 | 07-06-2011 | OK | OK |
| 19 | ADUAFOKWA DAM | 10.71 | 0.82 | 1.00 | 0.04 | 07-06-2011 | OK | OK |
| 20 | OTABILKWA BH | -4.72 | 0.60 | -2.41 | 0.07 | 07-06-2011 | OK | OK |
| 21 | F. BAWYAWASI BH1 | -10.78 | 1.03 | -2.14 | 0.10 | 07-06-2011 | OK | OK |
| 22 | KWEIKROM HDW | -5.82 | 0.74 | -1.44 | 0.19 | 07-06-2011 | OK | OK |
| 23 | OBOYOMBO HDW | -3.03 | 0.59 | -1.43 | 0.08 | 07-06-2011 | OK | OK |
| 24 | GYMZI | -11.95 | 0.48 | -2.70 | 0.05 | 07-06-2011 | OK | OK |
| 25 | BRAHA BH | -7.16 | 0.51 | -2.05 | 0.02 | 07-06-2011 | OK | OK |
| 26 | KWESIKUKWA BH | -2.55 | 0.99 | -1.19 | 0.13 | 07-06-2011 | OK | OK |
| 27 | KOKWAKO BH | -9.71 | 0.27 | -2.31 | 0.06 | 07-06-2011 | OK | OK |
| 28 | KYEREBUAKWA BH | -7.45 | 0.52 | -2.48 | 0.10 | 07-06-2011 | OK | OK |
| 29 | DOMINASE HDW | -4.49 | 0.55 | -1.93 | 0.06 | 07-06-2011 | OK | OK |
| 30 | R. OBOYAMBO | -1.44 | 0.17 | -1.45 | 0.14 | 07-06-2011 | OK | OK |
| Averages | | | 0.67 | | 0.11 | | OK | OK |

**APPENDIX 9.** Photographs of sampling sites and sponsors of some of the boreholes in the study area



Photograph of Ayensu river at Kwakwa in the dry season



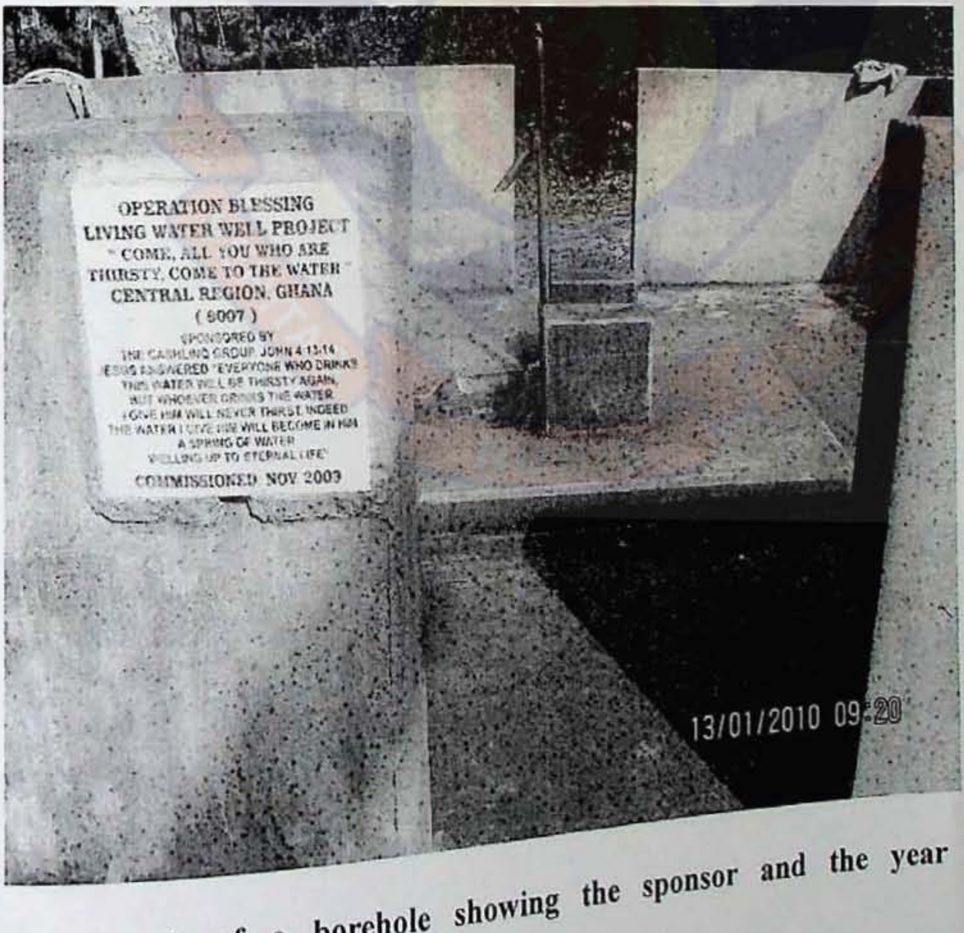
Photograph of Ayensu river during the raining season.

Photograph of a borehole showing the sponsor and the year of commissioning.

Photograph of a hand dug well showing the sponsors.

15/01/2010 11:52

Photograph of another borehole showing the sponsor and the year of commissioning.



13/01/2010 09:20

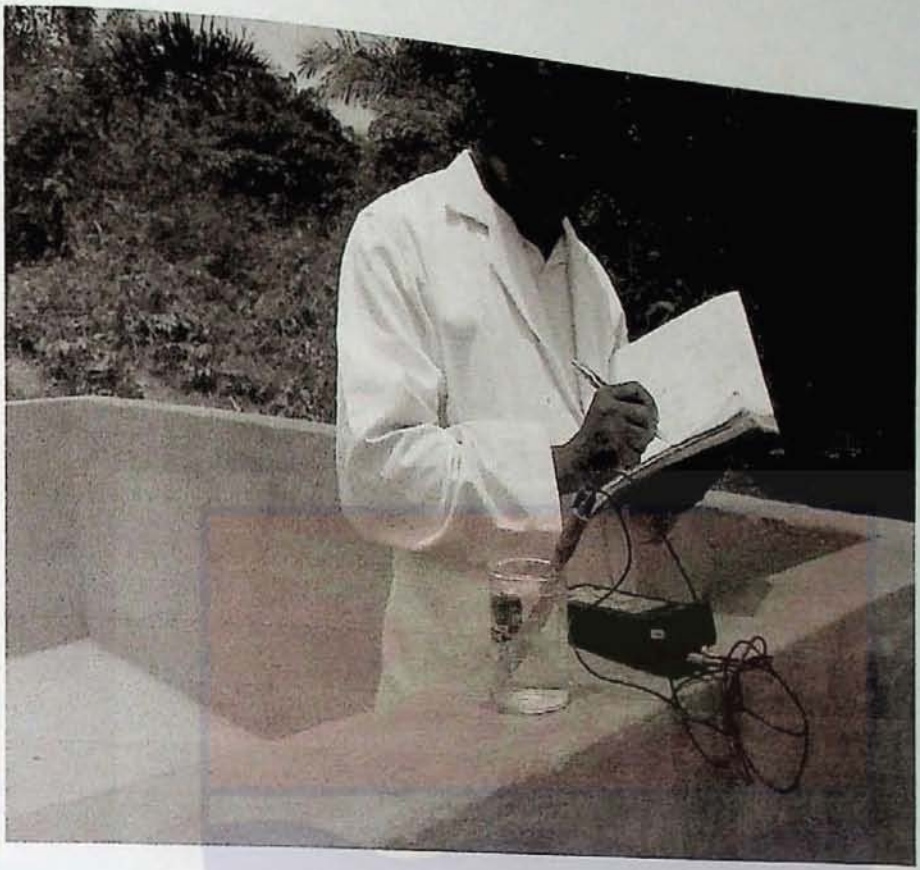
Photograph of a borehole showing the sponsor and the year of commissioning.

Photograph of the pond at Ojobi

Photograph of the stream at Awutu Kwabenya in the raining season.

Photograph of a Borehole near a cocoa farm.

Photograph of the stream at Obosomase.



**Photograph of pH, TDS and conductivity determination in the field using a portable meter.**