

UNIVERSITY OF GHANA

THE ORIGIN AND HYDROCHEMICAL EVOLUTION OF GROUNDWATER
IN THE LAKE BOSUMTWI AREA, GHANA

A THESIS SUBMITTED

BY

YVONNE SENA AKOSUA LOH

(10048068)

This thesis is submitted to the University of Ghana, Legon, in partial fulfilment of the requirement for the award of PhD Geology degree.

JUNE, 2014

ABSTRACT

Lake Bosumtwi is an important natural inland freshwater meteorite crater lake due to its scientific and socio-economic importance to both local and international communities. Although groundwater has been the main source of water supply for people living around the lake and visitors/tourists, very little work has been conducted with regard to the quality of the groundwater delivered by the aquifers within the lake basin. These aquifers are made up of the metasediments of the Birimian Supergroup and boreholes that are mostly fitted with pumps tap the groundwater.

A combination of conventional graphical methods, multivariate statistical and mass balance models have been applied to surface water in Lake Bosumtwi and groundwater hydrochemical and stable isotope ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) data from Birimian aquifers around the lake. The objective was to contribute to and improve the understanding of the hydrochemistry of the lake water and groundwater in aquifers around the lake and also to understand the relationship between these two reservoirs.

Results indicate that groundwater is of good to excellent quality for domestic use and is generally suitable for irrigation in comparison to the lake water that has high salinity and high sodicity and is, therefore, not suitable for irrigation. Hydrochemical and isotopic (i.e., $\delta^2\text{H}$ and $\delta^{18}\text{O}$) compositions of the groundwater and lake water suggest that there is no apparent incipient hydraulic relationship, which benefits the main aquifer system in terms of recharge from the lake. However, the reverse process, whereby the lake receives contribution from the aquifers through subsurface flow cannot be discounted on the basis of the data from this research.

Recharge of the aquifers appears to occur on hilltops where the water is characteristically acidic with low level of mineralization, suggesting short residence time. The groundwater within the basin has been recharged by recent meteoric water that has undergone evaporative enrichment prior to recharge. Evaporative loss in the range of 45% to 51% has been estimated for rainwater available for infiltration and subsequent recharge. The lake water is considerably enriched relative to the heavier isotopes of hydrogen and oxygen as a result of severe evaporation over the open lake surface. Estimated evaporative loss over the lake surface is about 82% resulting in the concentration of the univalent cations in the Lake.

Q-mode hierarchical cluster analysis (HCA) of the hydrochemical data employed to examine the spatial distribution of the investigated samples resulted in four spatial clusters (C1 to C4). Conventional graphical plots of the hydrochemical compositions of these clusters combined with mass balance hydrochemical modelling suggested that the groundwater has evolved from Na-Mg rich water types located on hill tops to Ca-Mg rich hydrochemical facies at the lower reaches of the crater. The relevant reactive minerals within the aquifers and the geochemical processes that control the hydrochemical evolution of the groundwater and lake water were also determined. R-mode principal component analyses (PCA) of the hydrochemical data suggested dissolution of aluminosilicates followed by carbonate mineral weathering and finally anthropogenic activities as the principal processes that influenced the hydrochemistry. Mineral stability diagrams suggested kaolinite as the most stable clay mineral phase in the groundwater system thus the groundwater in the area is generally at the intermediate stage in the evolution processes. In addition to dissolution of silicates, the chemical composition of the lake appears to have been influenced by evaporation and consequent saturation of carbonate minerals. The research has

demonstrated that an understanding of the hydrogeochemistry and the relationship between the lake and groundwater is important for environmental management.

ACKNOWLEDGEMENT

I am grateful to the Almighty God who granted me wisdom and strength to complete this task.

This work has been partly supported by ORID, through the Faculty Development Grant Award, the Department of Earth Science Capacity Building Project, University of Ghana and the University of Rochester, New York. I am also grateful to the Ghana Geological Survey Department for availing to me the accommodation facilities at Mmrontuo during the fieldwork.

My deepest appreciation goes to Prof. M. S. Yidana, who guided me with keen interest during the course of this investigation and for his helpful criticism and suggestions during the preparation of this thesis. Prof. D. K. Asiedu; I say "ayeekoo" for taking time off his busy schedule and offering helpful suggestions in my write up. Dr. P. A. Sakyi, your excellent suggestions, ideas and guidance are priceless. Prof. B. Banoeng-Yakubo, you have been very instrumental in sourcing funds to make this work a success. May God richly bless you. I am also greatly indebted to Profs. A. Basu and C. Garziona and Dr. P. Higgins, all of the Department of Earth and Environmental Science, University of Rochester, for allowing me to use the laboratories and helping me with the analysis of my samples.

Special thanks to E. Klubi, J. Mensah and K. Gyasi for assistance during sample collection. Thanks to my family for the encouragement, support and inspiration they offered during my studies. Ann, you were there at the time that I needed you most. George, I appreciate you so much, God bless you. I have also benefited from the knowledge, help and advice of so many friends, and colleagues who for want of space I cannot fit their names into a short preface. I hope you know yourselves and accept my appreciations.

TABLE OF CONTENTS

DECLARATION	i
ABSTRACT.....	ii
ACKNOWLEDGEMENT	v
LIST OF FIGURES	ix
LIST OF TABLES	xi
CHAPTER ONE.....	1
BACKGROUND AND INTRODUCTION	1
1.1 Background	1
1.2 Research Objectives	4
1.3 Scope and Limitations	4
1.4 The Study Area.....	6
1.4.1 Geography.....	6
1.4.2 Geology and hydrogeology.....	7
References.....	12
CHAPTER TWO	16

CHARACTERISATION AND QUALITY ASSESSMENT OF SURFACE AND
GROUNDWATER IN AND AROUND LAKE BOSUMTWI, GHANA 16

Abstract 16

2.1 Introduction 16

2.2 Materials and Methods 18

2.3 Results and Discussions 20

2.3.1 General hydrochemical Distribution 20

2.3.2 Hydrochemical Facies 23

2.3.3 Groundwater quality assessment for domestic use 28

2.3.4 Irrigation Water Quality 33

Conclusions 38

References 39

CHAPTER THREE 46

HYDROGEOCHEMICAL EVOLUTION AND STABLE ISOTOPE CHARACTERISTICS OF
GROUNDWATER AND SURFACE WATER IN LAKE BOSUMTWI, GHANA 46

Abstract 46

3.1 Introduction 47

3.2	Materials and Methods	50
3.3	Results and Discussions	53
3.3.1	Major ion chemistry	53
3.3.2	Stable Isotopes	61
	Conclusions	74
	References	75
	CHAPTER FOUR.....	85
	DETERMINATION OF THE MINERAL STABILITY FIELD OF EVOLVING GROUNDWATER IN THE LAKE BOSUMTWI IMPACT CRATER AND SURROUNDING AREAS	85
	Abstract	85
4.1	Introduction	86
4.2	Materials and Methods	88
4.3	Results and Discussions	90
4.3.1	Controls on groundwater and lake water hydrochemistry	99
	Conclusions	108
	References	109

CHAPTER FIVE	116
CONCLUSIONS AND RECOMMENDATIONS	116
5.1 Conclusions	116
5.2 Recommendations	117
References	119

LIST OF FIGURES

Fig. 1.1: Map showing the location of study area (after Jones et al., 1981; Reimold et al., 1998)	2
Fig. 1.2: Relief map of the study area (after Jones et al., 1981; Reimold et al., 1998).....	8
.....	8
Fig. 1.3: Geological map of the study area showing sample points (after Jones et al., 1981; Reimold et al., 1998)	9
Fig. 2.1: Boxplot of physical and chemical parameters for the various water samples.....	21
Fig. 2.2: Percentage frequency distribution of the major ion concentrations in the groundwater samples.....	22
Fig. 2.3: Chadha diagram showing the hydrochemicalfacies of the study area.....	24
Fig. 2.4: Gibbs diagram showing the positions of the water samples in the study area.	25
Fig. 2.5: Scatter plot of $(\text{SO}_4^{2-} + \text{HCO}_3^-)$ versus $(\text{Ca}^{2+} + \text{Mg}^{2+})$ for the samples	28
Fig. 2.6: Boxplot of trace element distribution in the groundwater samples of the study area	29
Fig. 2.7: USSL diagram of Sodium hazard (SAR) versus Salinity hazard (EC) for the samples.	34

Fig. 2.8: A Wilcox diagram showing classification of irrigation water in the study area	37
Fig. 3.1: Box plot for the physical and major ions for the water samples from the study area	53
Fig. 3.2: Stiff diagrams for the mean concentration of the major ions in groundwater and lake water.....	54
Fig. 3.3: Dendrogram generated from HCA of hydrochemical data from groundwater and lake water showing associations between the samples.....	55
Fig. 3.4: Spatial distribution of EC ($\mu\text{S}/\text{cm}$) in relation to sample clusters. Arrows show direction of increasing EC.....	56
Fig. 3.5: Spatial distribution of pH (pH units) in relation to sample clusters. Arrows show direction of increasing pH.....	57
Fig. 3.6: Schoeller diagram showing the arithmetic mean of the major ions in each cluster	60
Fig. 3.7: Box plot of the stable isotope contents of the analyzed water samples.....	63
Fig. 3.8: A scatter diagram of $\delta^2\text{H} - \delta^{18}\text{O}$ of the samples analyzed in this study. Also shown are the GWML and LWML.	64
Fig. 3.9: A scatter diagram of $\delta^2\text{H} - \delta^{18}\text{O}$ of the samples along with the LEL.	66
Fig. 3.10: Relationship between EC and $\delta^{18}\text{O}$ for the groundwater and lake water	71
Fig. 3.12: Relationship between Elevation and $\delta^{18}\text{O}$ for the groundwater	72
Fig. 3.13: Relationship between Elevation and EC for the groundwater.....	73
Fig. 4.1: Box plot for the physical and major ions for the water samples from the study area	90
Fig. 4.2: Dendrogram generated from HCA of hydrochemical data from groundwater (Clusters 1 to 3) and lake water (Cluster 4) showing associations between the samples.....	91

Fig. 4.3: Map showing the spatial distribution of samples based on clusters	92
Fig. 4.4: Stiff diagrams from the mean of the major ions in the four clusters from the Q-mode HCA	93
Fig. 4.5: Piper trilinear diagram showing the hydrochemicalfacies according to their clusters in the area	94
Fig. 4.6: Plots of saturation indices (SIs) with respect to various phases versus field pH for both groundwater and lake water. Arrows show that the groundwater approach equilibrium with increasing pH.	97
Fig. 4.7: Scatter plot of TDS vrs TH showing the quality of the water based on TDS and TH ...	99
Fig. 4.8: Scatter diagram showing the relationship between a) TZ and $\text{Na}^+ + \text{K}^+$ and b) TZ and $\text{Ca}^{2+} + \text{Mg}^{2+}$	102
Fig. 4.10: Bivariate plots of $(\text{Ca}^{2+} + \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-)$ vrs $(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$ (meq/l) for all cluster samples	105
Fig. 4.11: Scatter diagram showing the relationship between a) $\text{Ca}^{2+} + \text{Mg}^{2+}$ and $\text{HCO}_3^- + \text{SO}_4^{2-}$; b) Ca^{2+} and HCO_3^- ; c) Ca^{2+} and SO_4^{2-} all in meq/l in the study area.	106

LIST OF TABLES

Table 2.1: WHO guideline values, weight and relative weight of each of the chemical parameters used for the WQI determination	30
Table 2.2: Classification categories of WQI (Sahu and Sikdar, 2008).....	31
Table 2.3: WQI and classification of groundwater from the Study area	33
Table 3.1: Statistical summary of the physico-chemical parameters of the clusters.	58
Table 4.1: Saturation indices of possible reactive mineral phases in the groundwater and lake water samples from the study area.....	95

Table 4.2: Results of R-mode factor analyses which presents a) Factor loadings of the final factor model after varimax rotation; b) Communalities of parameters; c) Variance explained by the factors in the factor model 100

CHAPTER ONE

BACKGROUND AND INTRODUCTION

1.1 Background

Lake Bosumtwi, a scenic natural inland freshwater meteorite crater lake, is located in the Ashanti Region of Ghana (Fig. 1.1). Located in a unique and attractive, partly forested area, it serves as a regional tourist site (Boamah and Koeberl, 2007). The Lake Bosumtwi area is an important geological site because it houses the largest, young (1.07 Ma) and well-preserved complex meteorite impact crater currently known on earth. The interior of the crater is filled by an 8 km wide Lake, Bosumtwi, which is 78 m deep and represents the only significant natural lake in Ghana and the West African subregion (Scholz et al., 2007). Several communities surrounding the lake have historically depended solely on fish catch from the lake as an important source of livelihood and also relied on perennial streams that flowed into the lake for drinking and domestic water supply needs. As the fortunes in fishing declined due to mass deaths of fish (Turner et al., 1996) and over fishing from a growing population (Prakash et al., 2005) more people have turned to cultivation of all kinds of crops and livestock rearing as alternative sources of food and income. Besides fishing and livestock watering, the people use this resource to provide other social and economic opportunities such as transportation and local tourism. In recent times, the sustainable socio-economic development of the people within this basin is tied, among other things, to eco-tourism. With the tremendous increase in local tourism activities, the area has been earmarked to be developed into a geological heritage site (Boamah and Koeberl, 2007).

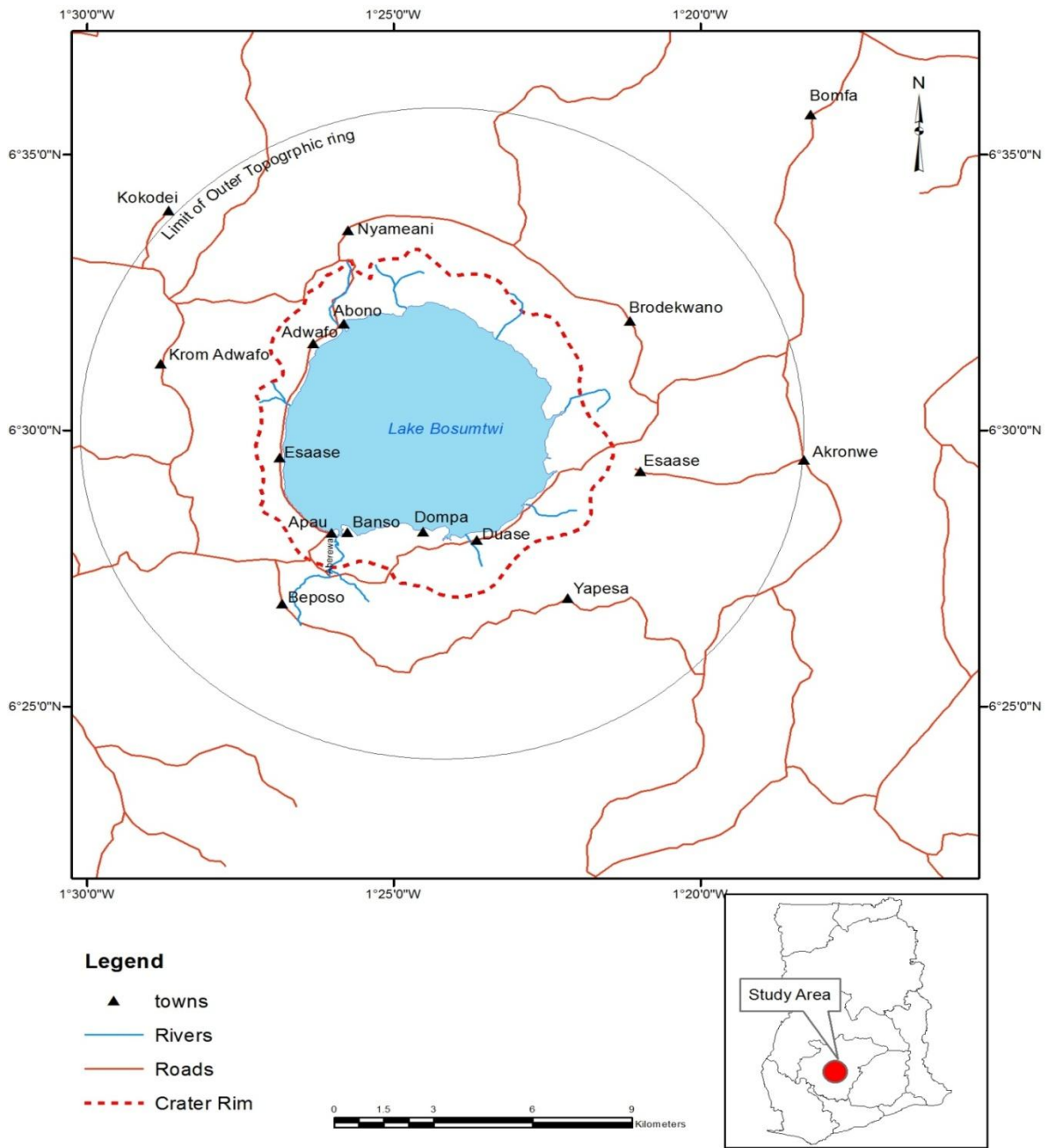


Fig. 1.1: Map showing the location of study area (after Jones et al., 1981; Reimold et al., 1998)

The combined effect of changing land use patterns, growth in population leading to a rise in human activities and climatic variability have caused most of the perennial streams to become polluted and ephemeral resulting in water scarcity and its accompanying water borne diseases. Consequently, the Government of Ghana and non-governmental organizations (e.g. Madamfo Ghana) have provided these communities with boreholes drilled through weathered and fractured aquifer at various depths within the basin that discharge groundwater for drinking and domestic use of the people. Although groundwater is better protected from surface polluting activities, and is, therefore, bacteriologically more suitable for most domestic and irrigation uses without prior chemical treatment, like surface water, groundwater can be contaminated. Its integrity, security and sustainability could be compromised by anthropogenic activities and developments such as waste from intensive livestock operation, fertilizers and pesticides, oil and other spills and leaky underground storage/sewage tanks.

Several activities that may compromise the aesthetic beauty of the lake and pose serious environmental degradation that may stall eco-tourism development within the Basin have been discussed (Prakash et al. 2005). Boamah and Koeberl (2007) have reported a sudden rise in the chain of hotels and proliferation of tourism facilities by individuals in the lake basin in an uncoordinated manner. It is, therefore, important that pragmatic measures are taken to protect the integrity of the surface water in the lake and groundwater bodies in the area. This requires a comprehensive appraisal of the available surface and groundwater resources. Such studies would assist in constructing and analysing the historical hydrogeology of the area, and possible evolution that have occurred in the groundwater chemistry since the meteorite impact. This study initiates such an endeavour in the area.

In the face of inadequate fundamental data on groundwater flow patterns and aquifer characteristics from the study area, this research applied a combination of statistical, graphical techniques and hydrochemical models on hydrogeochemical and isotope data to determine the main factors that control the hydrochemistry of both lake water and groundwater and examined their quality for domestic and irrigation use. In addition to assessing the general sources of variation in the hydrochemistry, evolutionary patterns and any possible hydraulic connection between surface water in the lake and groundwater in aquifers around the latter were investigated.

1.2 Research Objectives

The research aimed at evaluating the hydrochemistry of groundwater and lake water in the area to support the utilisation of these resources in a sustainable manner. Specifically, this study will:

- Determine the main factors that control the hydrochemistry of both lake water and groundwater and thus elucidated on the hydrochemical evolution of groundwater in the area;
- Identify probable groundwater recharge areas and source of recharge to the aquifers
- Investigate the hydraulic relationship between groundwater in aquifers around the lake and surface water in the lake.

1.3 Scope and Limitations

In order to achieve the set objectives, lake water and groundwater in aquifers around the lake were sampled and analysed for major and minor ions by ICP-MS, ICP-OES and IC. The data

obtained was used to determine the hydrochemical facies, the suitability of both water resources for irrigation, and the quality of groundwater for drinking and other domestic use. The geochemical processes that control the chemical composition of these water resources, possible groundwater recharge areas, groundwater flow path and evolution were successfully determined from the data.

The flow path would have been better defined if static water levels were measured. It was however impossible to measure the static water levels since the boreholes are fitted with hand pumps and permit to dismantle them could not be obtained. Even if permit was granted, it will still have been impossible to take the measurement because of the time allotted for fieldwork, the distance to travel from one borehole to the other and financial constraints. Strontium isotope compositions of the groundwater could have provided additional information about the flow path. However, financial and time constrains hindered the analysis of this data.

The hydraulic relationship between the lake and groundwater and the source of water to these reservoirs were determined from the combined use of the physico-chemical data and stable isotopes of water molecule analysed for rainwater taken from the area and selected lake and groundwater samples. Within the limits of time and logistics only three rainwater and four lake water samples were analyzed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Thus all discussions and conclusions made with regard to the stable isotope content of rainwater and lake water in this thesis are based solely on these few data points. The mean lake residence time and groundwater-lake exchange could have been determined if enough seasonal variation of $\delta^{18}\text{O}$ data were obtained. This was not possible due to time and financial constrains.

The subsequent chapters thus present three manuscripts that discussed the use of hydrogeochemical and isotopic data of the lake water and groundwater resources to obtain hydrogeological information from the area. Chapter two (manuscript 1) characterized the water resources in the study area regarding major cations and anions. The quality of the water is evaluated using conventional methods and the general distribution of hydrochemistry and the suitability of water resources for various uses have been discussed.

Chapter three (manuscript 2) discussed the use of hydrochemical and environmental isotope data of water as natural tracers for the geochemical evolution of both groundwater and lake water. Possible recharge areas and hydraulic relationship between the lake and the aquifers surrounding the former were investigated. Also the stable isotopes were used to calculate the possible evaporation rates of rainwater before or during replenishment of the various water reservoirs.

The geochemistry of the lake water and groundwater including the hydrogeochemical classification of the basin has been discussed in Chapter four (manuscript 3). It also discussed the chemical characteristics of the waters, controls on the waters, and the hydrochemical evolution of the groundwater. Phreeqc was used to calculate ionic speciation and ion activities from which stability diagram were made to suggest the most stable mineral phase. The final chapter (Chapter five) presents the conclusions and the recommendations for further work.

1.4 The Study Area

1.4.1 Geography

The physical structure of the crater has been well described in various literatures (Jones et al., 1981; Karp et al., 2002). The impact crater has a steep rim rising up to 300 m above present lake

level. It is surrounded by an irregular circular depression forming a hydrologically closed basin with a rim-to-rim diameter of 10.5 km, as well as an outer ring of minor topographic highs with a diameter of about 20 km (Jones et al., 1981; Reimold et al., 1998) (Fig. 1.2). Characterised by a tropical rain forest environment, the climate is semi-equatorial with double maxima rainfall pattern between 1600 mm and 1800 mm with an average of about 150 rainy days in a year. The first major rainfall season starts from March and ends in July with a peak in June whilst the second rainfall season starts from September to November and peaks in October. The climate is warm with a fairly high and uniform temperature ranging from 32°C in March and 20°C in August. Relative humidity ranges between 70 and 80 percent (Turner et al., 1996). The original vegetation cover of semi-deciduous and rainforest has been degraded to mosaic of secondary forest due to extensive and repeated farming, illegal mining and lumbering. The drainage pattern of Bosumtwi District is dendritic. However, around Lake Bosumtwi, there is an internal drainage where the streams flow from surrounding highlands into the lake forming a dense network due to the double maxima rainfall regime.

1.4.2 Geology and hydrogeology

Rocks of the Birimian Supergroup, made up of two major lithostratigraphic units: Birimian Sedimentary Basins and Birimian Volcanic Belts (Kesse, 1985) of early Proterozoic age underlie the study area (Fig. 1.3). These rocks host most of Ghana's mineral deposits (e.g. gold and

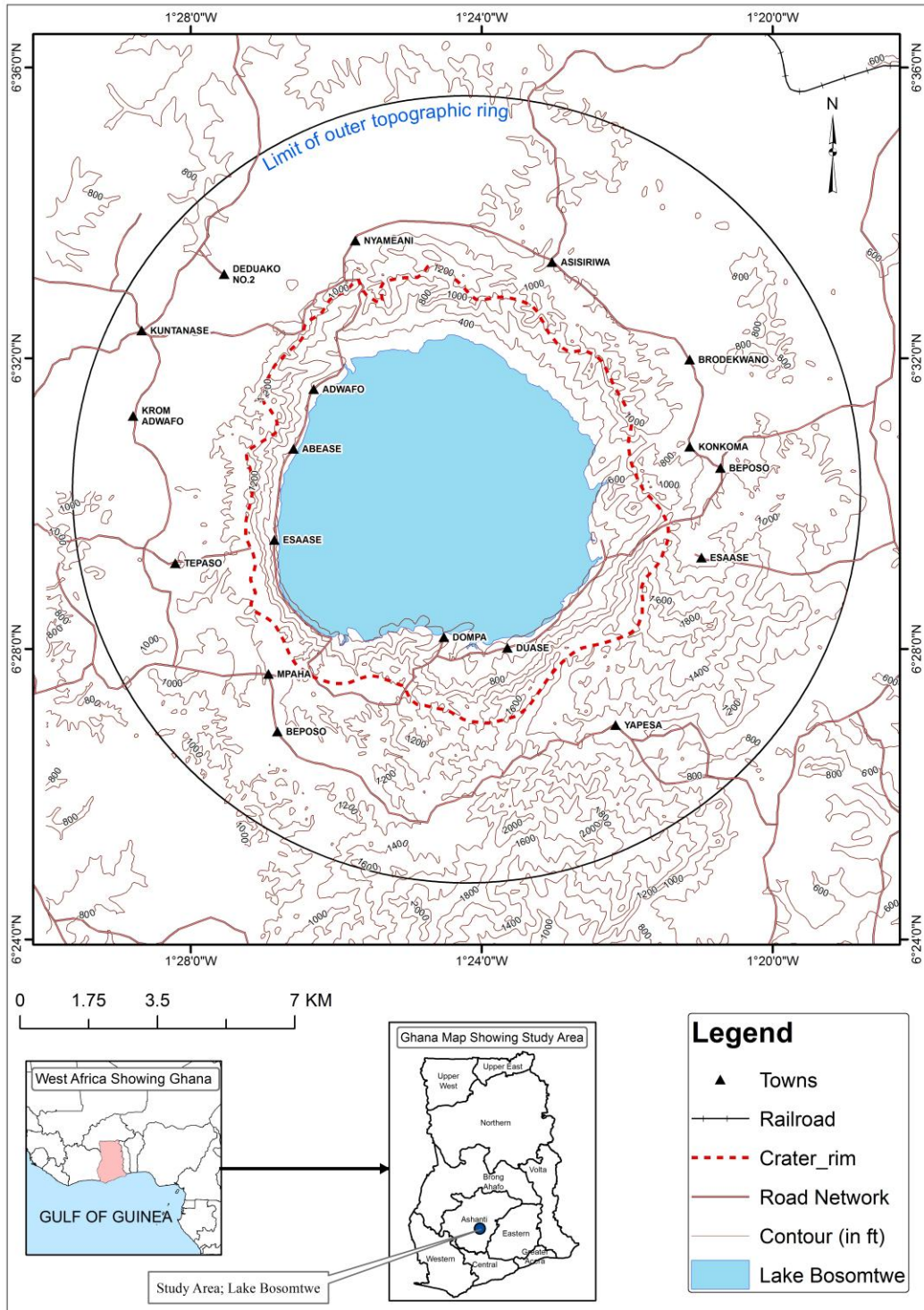


Fig. 1.2: Relief map of the study area (after Jones et al., 1981; Reimold et al., 1998)

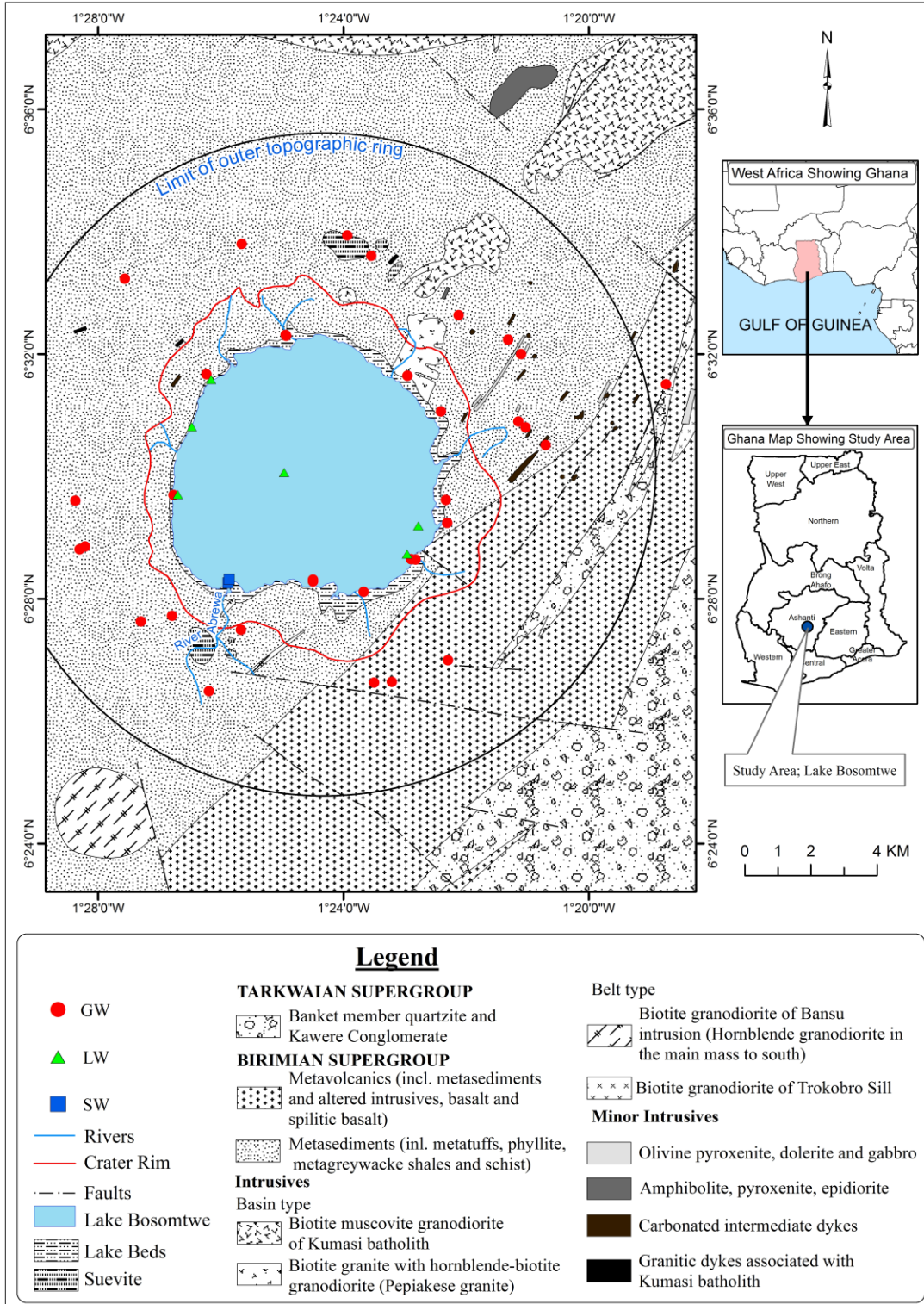


Fig. 1.3: Geological map of the study area showing sample points (after Jones et al., 1981; Reimold et al., 1998)

diamond) and have been extensively studied by various workers (Leube et al., 1990; Hirdes et al., 1992). These studies showed that the Eburnean tectonothermal event, which stabilized the West African Craton caused the Birimian Supracrustal rocks to become folded and metamorphosed under greenschist-facies conditions, and intruded by granitoids. The Bosumtwi Impact Crater (BIC) was formed in the greenschist facies metasedimentary rocks of the 2.0-2.2 Ga Birimian Supergroup, partly surrounded by numerous localized granitoid intrusions, of size mainly dikes of Biotite granitoid which are generally <1 m wide, occurring as basement exposures in the crater rim (Reimold et al., 1998). The most prominent intrusion located in the northeastern sector of the crater at Pepiakese, consists of a variety of rock types ranging from hornblende- to biotite-muscovite granite and dolerite (Koeberl et al., 1998). Rocks at and around Lake Bosumtwi are dominated by meta-sandstones, shales, phyllites, and schist (Leube et al., 1990; Hirdes et al., 1992). These metasediments are rich in quartz, feldspars (plagioclase and alkali feldspars), micas (biotite, muscovite). Exposures of metavolcanics and Tarkwaian metasedimentary rocks are located on the southeastern section of the crater. Recent publications (e.g. Koeberl et al., 1997; Koeberl et al., 1998; Reimold et al., 1998; Boamah and Koeberl, 2002; Karikari et al., 2007) provide detailed petrographical, mineralogical and geochemical studies on the lithologies of the Bosumtwi structure. Some of the accessory minerals in these rocks include, carbonates, Fe-oxides, secondary sericite and chlorite and some opaque minerals, notably sulphides (Karikari et al., 2007).

A detailed structural analysis (Reimold et al., 1998) along a complete traverse through the northwestern rim section concluded that outward-directed thrust faulting and intense folding characterise the middle and upper part of the BIC while the innermost crater rim is dominated

by intense thrust faulting of multiple orientation resulting in more complex, thrust-related features such as duplex thrusts forming lenses of faulted rock with generally inward-dipping bedding.

Secondary porosity and permeability in the rocks of the study area were created during the Eburnean orogenic event some 2.1 Ga ago (Kesse, 1985) and impact cratering (Reimold et al., 1998). The tectonic lines of weakness that developed during the Eburnean orogenic event and the lineaments that are associated with crater formation facilitated extensive and deep weathering of the rocks. Weathering is enhanced where the fractures, joints, faults, folds and quartz veins are many and dense. Groundwater occurrence and movement, particularly in hard rock terrains such as the study area, are multivariate and governed principally by these geological structures. Other factors that can influence groundwater occurrence and movement include topography, lithology, texture of parent rock and nature of weathering. The water-bearing and yielding capacities of these rocks depend on the extent of rock weathering, and the presence of quartz aplite and pegmatite veins as well as fracture openings (Banoeng-Yakubo, 2000). Thick weathered zones reaching depths of approximately 30 m to 50 m occur and are greatest in the Birimian rocks, and depths of up to 70 m have been discovered at certain places in rocks of the study area (Boamah and Koeberl, 2002). The rocks, especially the micaceous and feldspathic schists, usually weather to clays, which reduce the permeability. Geophysical (resistivity) studies for groundwater prospection in the region and well logs from boreholes and wells collated from consultants in the study area indicate that the stratigraphy of the aquifer is made up of 3 layers. These comprise upper, intermediate and lower layers of humic or lateritic soils, highly weathered rocks and moderately weathered to fractured fresh rocks respectively. However, the best aquifers with

relatively high yields are developed along the slopes of the synclinal troughs where significantly weathered materials have accumulated and within jointed and fractured phyllites, meta-graywackes and meta-volcanic quartz schists. Aquifers are also developed on hilltops characterized by local tension joints in the moderately weathered zones. Data collated from consultants on boreholes drilled within the morphological crater rim indicates that the boreholes tap water under semi-confined aquifer conditions from weathered and/or fractured meta-graywackes, phyllites, schists, and granites at varying depths of 26 m to 64 m averaging 43 m. The depth to water level in the area varies between 3 m to 43 m below ground level. Yields range from as low as 0.6 m³/h to about 9.0 m³/h with specific capacities in the range of 0.027 m³/h/m to 18.18 m³/h/m (Banoeng-Yakubo, 2010). Variation in the yields observed in the area depends on the topographic set up, lithology and degree of weathering.

References

- Banoeng-Yakubo, B. K., 2000. *The Application of Remote Sensing and Geographical Information Systems to Hydrogeological studies in the Upper West Region, Ghana*. (PhD Thesis). University of Ghana.
- Banoeng-Yakubo, B., Yidana, M.S., Ajayi, J.O., Loh, Y. and Asiedu, D.K., 2010. *Hydrogeology and groundwater resources of Ghana: a review of the hydrogeology and hydrochemistry of Ghana*. In: *Potable Water and Sanitation*. Joel M. McMann eds.: Nova Science Publishers, Inc. 77-114
- Boamah, D. and Koeberl, C., 2002. Geochemistry of Soils from the Bosumtwi Impact Structure, Ghana, and Relationship to Radiometric Airborne Geophysical Data. *In: Impacts in*

- Precambrian Shields*. Plado, J. and Pesonen, L. eds. Springer Berlin Heidelberg, 211-255.
- Boamah, D. and Koeberl, C. 2007. The Lake Bosumtwi impact structure in Ghana: A brief environmental assessment and discussion of ecotourism potential. *Meteoritics & Planetary Science*, 42(4-5), 561-567.
- Hirdes, W., Davis, D. W. and Eisenlohr, B. N. 1992. Reassessment of Proterozoic granitoid ages in Ghana on the bases of U/Pb zircon and monazite dating. *Precambrian Research*, 56, 89-96.
- Jones, W. B., Bacon, M. and Hastings, D. A. 1981. The Lake Bosumtwi impact crater, Ghana. *Geological Society of America Bulletin*, 92(6), 342.
- Karikari, F., Ferrière, L., Koeberl, C. Reimold, W. U., and Mader, D. 2007. Petrography, geochemistry, and alteration of country rocks from the Bosumtwi impact structure, Ghana. *Meteoritics & Planetary Science*, 42(4-5), 513-540.
- Karp, T., Milkereit, B. Janle, P., Danuor, S. K., Pohl, J., Berckhemer, H. and Scholz, C. A. 2002. Seismic investigation of the Lake Bosumtwi impact crater: preliminary results. *Planetary and Space Science*, 50, 735-743.
- Kesse, G. O., 1985. *The mineral and rock resources of Ghana*. Boston: Rotterdam, A.A. Balkema.

- Koeberl, C., Koeberl, C., Bottomley, R., Glass, B. P. and Storzer, D. 1997. Geochemistry and age of Ivory Coast tektites and microtektites. *Geochimica et Cosmochimica Acta*, 61(8), 1745-1772.
- Koeberl, C., Reimold, W. U., Blum, J. D. and Chamberlain, P. C. 1998. Petrology and geochemistry of target rocks from the Bosumtwi impact structure, Ghana, and comparison with Ivory Coast tektites. *Geochimica et Cosmochimica Acta*, 62(12), 2179-2196.
- Leube, A., Hirdes, W., Mauer, R. and Kesse, G. O. 1990. The early Proterozoic Birimian Supergroup of Ghana and some aspects of its associated gold mineralization. *Precambrian Research*, 46, 139-165
- Prakash, S., Wieringa, P., Ros, B., Poels, E., Boateng, F. S., Gyampoh, B. A. and Asiseh, F. 2005. *Potential of ecotourism development in the Lake Bosumtwi Basin: A case study of Ankaase in the Amansie East District, Ghana*. University of Freiburg: University of Freiburg, Germany, 1616-8062.
- Reimold, W. U., Brandt, D. and Koeberl, C. 1998. Detailed structural analysis of the rim of a large, complex impact crater: Bosumtwi Crater, Ghana. *Geology*, 26, 543-546.
- Scholz, C. A., Karp, T. and Lyons, R. P. 2007. Structure and morphology of the Bosumtwi impact structure from seismic reflection data. *Meteoritics & Planetary Science*, 42(4/5), 549-560.

Turner, B., Gardner, L. Sharp, W. and Blood, E. 1996. The geochemistry of Lake Bosumtwi, a hydrologically closed basin in the humid zone of tropical Ghana. *Limnology and Oceanography*, 41(7), 1415-1424.

CHAPTER TWO

CHARACTERISATION AND QUALITY ASSESSMENT OF SURFACE AND GROUNDWATER IN AND AROUND LAKE BOSUMTWI, GHANA

Abstract

Conventional graphical methods have been used to classify water in Lake Bosumtwi and groundwater around the lake. The study also assessed the suitability of these water resources for agricultural use. Results indicate slightly acidic, moderately hard to very hard groundwater with alkaline earths concentrations exceeding alkali metals. In contrast, the Lake water is alkaline showing alkalis in excess over alkaline earths. Weak acids exceed strong acids in both lake and groundwater. Mineral weathering largely controls the lake water and groundwater resulting mainly in Ca-Mg-HCO₃ groundwater and Na-HCO₃ lake water types. Water quality indices suggest groundwater of good to excellent quality for human consumption and other domestic use. An evaluation of lake and groundwater based on sodium adsorption ration (SAR), sodium percent and residual sodium carbonate (RSC) reveal that the groundwater is generally suitable for irrigation whiles the lake water is not. However, the lake water may be used on highly permeable soils and salt tolerant crops under special soil and water management practices.

2.1 Introduction

The use of hydrochemical datasets in hydrological and hydrogeological studies to characterise water resources, establish hydrological relationships and to track hydrological processes is conventional practice. For instance, researchers have utilized such datasets in characterising the hydrogeology of watersheds, trace groundwater flow paths in aquifers (Flusche et al., 2005;

Rouabhia et al., 2009) and to evaluate water quality (Milovanovic, 2007; Yidana et al., 2008; Anku et al., 2009). The approach is based on the fact that certain chemical characteristics of water bodies are essential indications of the sources and evolution processes of the water in transit. Careful analyses of the variations in such parameters in the light of the underlying lithology, vegetation, and climatic conditions provide very useful leads to the evolutionary trends of groundwater. Through this methodology, distinct groundwater flow paths have been defined to assist in conceptualization of hydrological systems and processes (Schilling et al., 2006).

Lake Bosumtwi has attracted international attention due to its scientific value. Much of the research in the basin has been focused on establishing its origin and evolution through time (Jones, 1985; Koeberl et al., 2007a; Koeberl et al., 2007b). Although the people living around the lake have depended on groundwater for their drinking and domestic purposes over the years, very little work has been done with regards to the quality of groundwater resources within the basin. Various authors (Milovanovic, 2007; Yidana et al., 2008; Anku et al., 2009), however, concur that water of good quality is essential for good health, ecosystems, economic development and social prosperity. Previous studies on the water resources within the basin focused on the hydrology and geochemistry of the lake and streams (McGregor, 1937; Turner et al., 1996a; Turner et al., 1996b). In recent times, Adu et al. (2011) assessed the water quality with emphasis on the radionuclide concentrations of the lake and the groundwater. However, the physical and hydrogeochemical properties of both surface water in the lake and groundwater in the surrounding aquifer have not been studied. In this paper, the physico-chemical parameters of lake and groundwater samples will be studied to classify these water resources into hydrochemical facies and determine their suitability for a variety of uses. The physical and

chemical character of the groundwater will be evaluated in terms of water quality index (WQI) to determine its suitability for drinking and other domestic uses. This index is very effective in communicating to consumers and policy makers on the quality of drinking water and also serves as an important parameter in the assessment and management of drinking water. As many countries, including Ghana, are moving away from rain-fed peasant farming to a more mechanized irrigated commercial farming to meet the global demand for food, the study will also assess the suitability of both lake and groundwater for irrigation use. Finally, since groundwater moves with very low velocities, degradation in quality may take a considerable length of time to notice and with the current trend of human activities within the basin, it is envisaged that the quality of the water resources could be compromised. This research will thus establish background conditions (pristine or anthropogenically altered) on the quality of lake and groundwater resources within the basin needed by policy makers to make more informed water policy decisions.

2.2 Materials and Methods

A total of 43 water samples (34 groundwater samples, 7 lake water samples and 2 stream samples) (Fig. 1.3) used in this study were collected in a relatively cool and dry period spanning July 20 to August 5, 2012. The only stream, Abrewa, (Fig. 1.3), flowing into the lake at the time of sampling, was sampled at the point of entry into the lake and at another point about 150 m from the lake. In an attempt to collect only samples that were representative of the aquifer, the boreholes were purged and sampled only when either EC or pH became steady with time. The water samples were filtered through a 0.45 μm cellulose acetate membrane and collected in 50-ml sterilized polypropylene tubes in two sets; one was acidified with pure nitric acid (HNO_3^-) to

pH <2 for major cations and trace element analyses while the other unacidified filtered samples were used for anion analysis. Acidification restricts bacterial action, blocks oxidation reactions, and also prevents adsorption or precipitation of cations (Chapman, 1996). Prior to collection, the sample tubes were first rinsed with distilled water and later with portions of the filtrate before they were filled. Collected samples were tightly capped and sealed with an electric insulating tape and were clearly labelled to distinguish acidified samples from unacidified ones. The samples were stored in ice in separate boxes and later transported to the USA for laboratory analysis. The coordinates (latitude and longitude) and elevations of sample sites were taken using a hand-held Garmin-eTrex Vista HCx global positioning system (GPS). For all samples collected, physical parameters such as electrical conductivity (EC), total dissolved solids (TDS), salinity (Sal), water temperature (T), pH, oxidation- reduction potential (ORP), and dissolved oxygen (DO) of sampled water sources were measured in situ using a HI 98280 GPS Multiparameter Meter manufactured by HANNA Instruments. The alkalinity (Alk) (as HCO_3^-) was measured with the Hatch digital titrator in the field. A water sample location map showing the spatial distribution of sample points was generated from the GPS locations using ArcGIS ArcMap10 (Fig. 1.3). Inductively Coupled Plasma- Mass Spectrometer (ICP-MS) at Activation Laboratories Ltd in Canada determined the major cations and trace elements. Samples that were above the specified range (i.e. > 25 ppm of Na, K, and Sr; and > 100 ppm of Ca, Mg and Si) were reanalyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) in milligram per liter (mg/l). Using Dionex DX 120 ion chromatograph (I.C), anions of Chloride (Cl^-), sulphate (SO_4^{2-}), and nitrate (NO_3^-), fluoride (F^-), nitrite (NO_2^-), and phosphate (PO_4^{3-}) in milligram per liter ((mg/l) were analysed. Charge balance error (CBE) calculated (Equation 2.1)

to check the accuracy of the laboratory (analytical) results was generally within $\pm 10\%$ on the basis of ions expressed in meq/l (Appelo and Postma, 2005).

$$CBE = \frac{\sum Cations - \sum Anions}{\sum Cations + \sum Anions} \times 100\% \dots\dots\dots 2.1$$

Various statistical methods were subsequently applied to the data set using SPSS, Microsoft Excel and other softwares with statistical packages to assess the variables independently and determine the relationships between variable pairs.

2.3 Results and Discussions

2.3.1 General hydrochemical Distribution

Figure 2.1 presents box and whisker plots of the physico-chemical parameters measured in the stream, groundwater and lake water samples. In general, the mean values calculated for most of the measured parameters are within the World Health Organisation (WHO, 2011) acceptable limits for domestic and irrigation use. The pH range of 5.08 to 7.25 with a mean of 6.37 classifies the groundwater as slightly acidic. The lake water is alkaline with a pH range of 8.39 to 9.06 and a mean pH value of 8.86. The slight acidity of the groundwater in aquifers located in an area that is covered by dense tropical rainforest; high rainfall, warm climate and high organic activity is expected and may have resulted from the direct infiltration of rainwater and natural biogeochemical processes. The electrical conductivity (EC) values of the groundwater from the area are generally low, ranging from 138 $\mu\text{S}/\text{cm}$ to 1746 $\mu\text{S}/\text{cm}$ with a mean of 623 $\mu\text{S}/\text{cm}$. The lake water, on the other hand, has a mean EC value of 1313.29 $\mu\text{S}/\text{cm}$, ranging from 1262 $\mu\text{S}/\text{cm}$ to 1344 $\mu\text{S}/\text{cm}$. The TDS concentration of the Lake water varies between 634 mg/l and 672 mg/l

averaging 657 mg/l and the bicarbonate ion concentration is in the range of 500 mg/l to 526 mg/l with a mean of 514.43 mg/l. The ion concentration percent frequency diagrams (Fig. 2.2) are useful in defining the relative concentration of cations or anions as percentages of total cations and anions respectively (Kortatsi, 2006). Results of the analyses of the groundwater presented (Fig. 2.2) show that sodium, calcium and magnesium ions are fairly represented and no cation dominates in the groundwater except in a few cases where these cations extend to the zone of dominance (i.e. % meq/l > 50). Among the major cations, however, Na⁺, on the average amounts to about 37% in abundance, followed by Ca²⁺ which is approximately 32% with Mg²⁺ and K⁺,

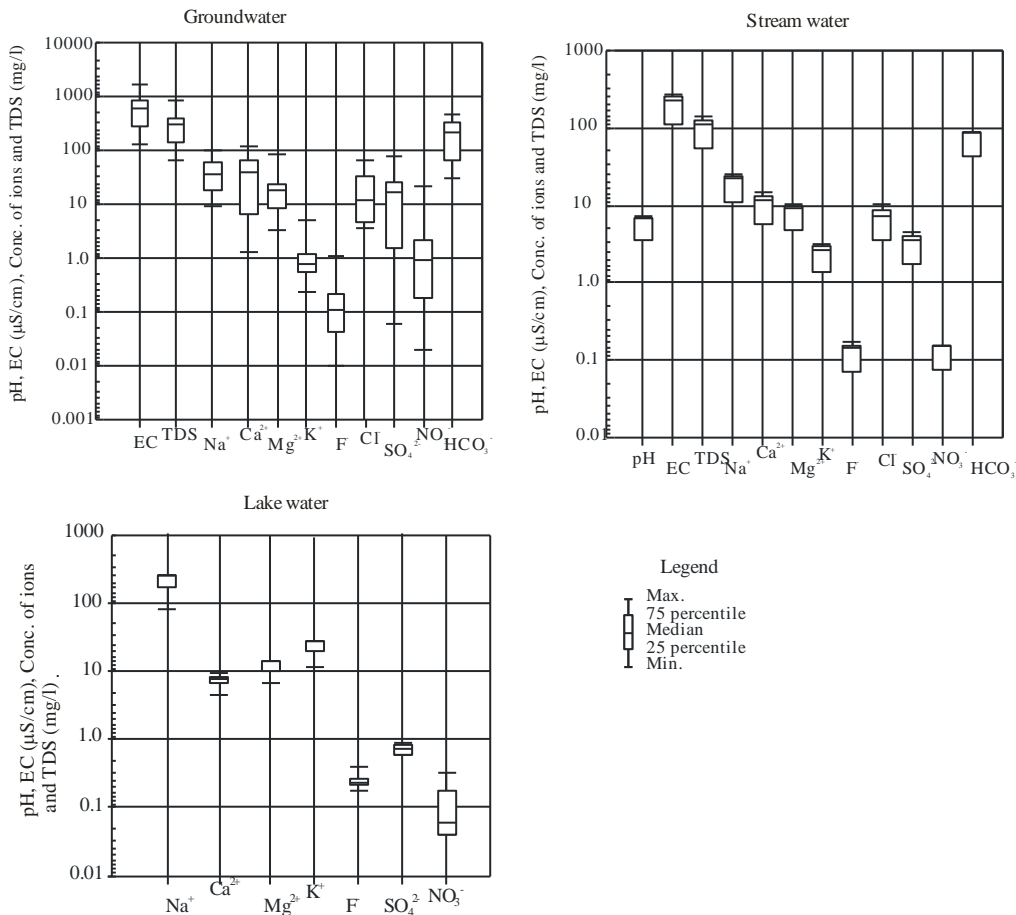


Fig. 2.1: Boxplot of physical and chemical parameters for the various water samples

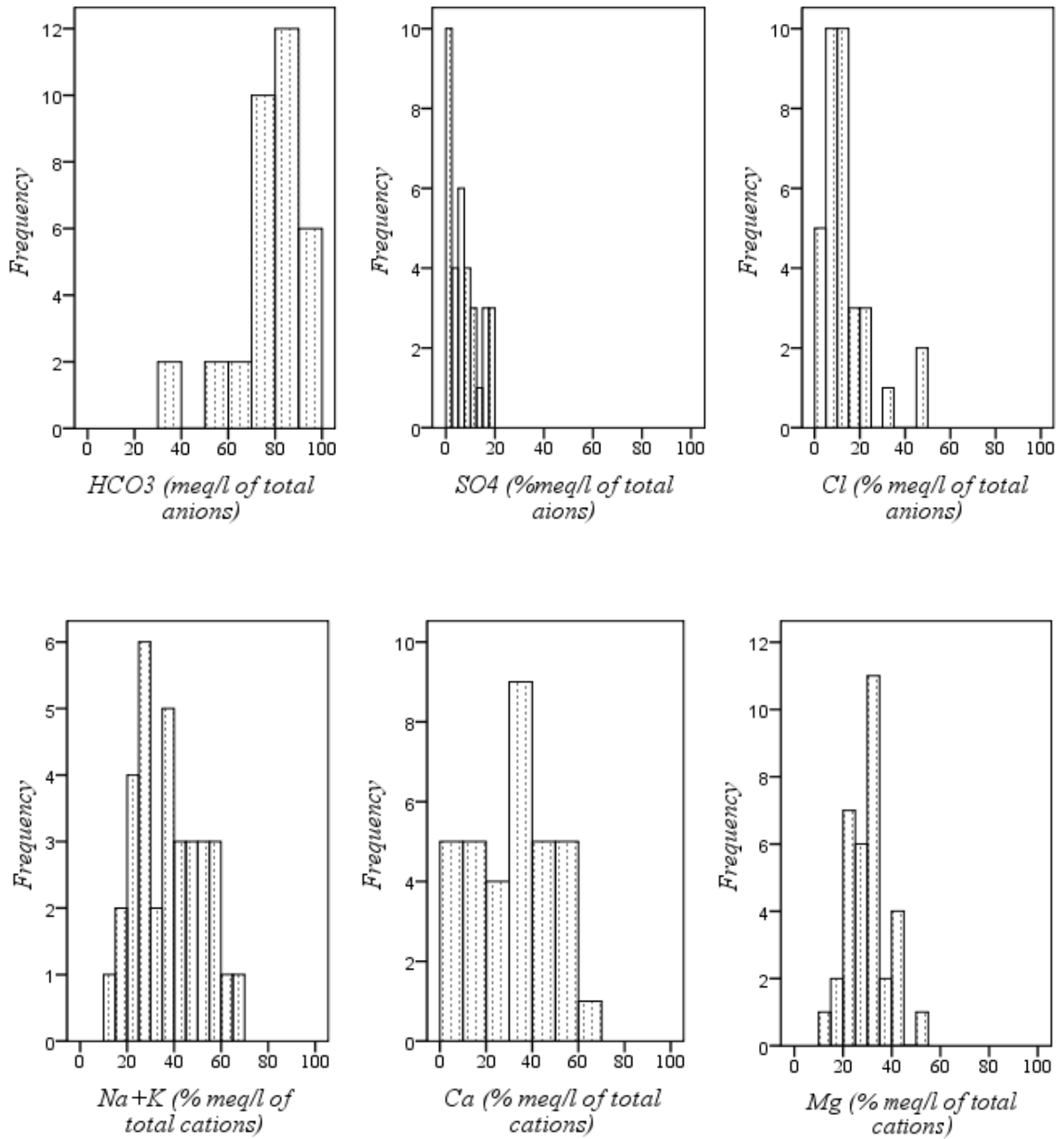


Fig. 2.2: Percentage frequency distribution of the major ion concentrations in the groundwater samples

respectively, representing 30% and 1% of the total cations. Bicarbonate (HCO_3^-) ions, among the major anions, constitute about 78% of total anions followed by Cl^- ions, (14%) with SO_4^{2-} ions representing 7%.

On the other hand, Na^+ alone contributes as much as 82% of total cations with Mg^{2+} , K^+ and Ca^{2+} , respectively, representing 9%, 6% and 3% in the lake while HCO_3^- and Cl^- , dominate the major anions with relative percentage contribution of about 73% and 27% respectively of total anions in the lake. The order of relative abundance of major cations in the groundwater samples is $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+}$ while that of the anions is $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ thus bicarbonates of calcium, magnesium and sodium generally dominate the groundwater and lake.

2.3.2 *Hydrochemical Facies*

The Chadha diagram (Chadha, 1999) (Fig. 2.3) was used to classify the overall chemical character of the water from the study area and used to conceptualize the possible relationship between the lake water and groundwater. Figure 2.3 shows that the samples collected from the stream and about 76% of groundwater samples have alkaline earths ($\text{Ca} + \text{Mg}$) exceeding alkali ($\text{Na} + \text{K}$) metals. The remaining 24% of groundwater samples and all the lake water samples show an excess of alkali metals over the alkaline earth metals. Almost all the water samples except two (2) groundwater samples located at Timeabu (HW001) and Beposo (GW041) have weak acid (HCO_3^-) in excess of the strong acids ($\text{SO}_4^{2-} + \text{Cl}^-$). The overall enrichment of the groundwater with bicarbonate relative to chloride or sulphate may be attributed to freshwater recharge by rainwater through the overburden. Bicarbonate ion concentration in groundwater generally result when silicate minerals weather in the presence of a weak carbonic acid obtained from rainwater (Appelo and Postma, 2005). The stream water and majority (~70%) of the

groundwater samples are Ca-Mg-HCO₃ water types. The remaining groundwater samples plot in fields defined by the Na-HCO₃, Na-Cl and Ca-Mg-HCO₃-Cl (Fig. 2.3), representing 18%, 6% and 6% respectively of the total groundwater. The lake water is characteristically Na-HCO₃ water type. The facies relationships (Fig. 2.3) and the general concentrations of the major hydrochemical parameters indicate an apparent evolution of water from a relatively low concentrated groundwater to relatively more concentrated lake water. This implies that any hydraulic connection between lake water and groundwater encourages groundwater discharge into the lake and not vice versa. Regarding the comparatively high total dissolved solids content of the lake water relative to groundwater in the area; it is not possible to have had contributions of lake water to groundwater recharge under the prevailing hydrologic conditions in the area. Therefore, within the limits of the groundwater outlets sampled for this study, there is no apparent suggestion of any incipient relationship that benefits aquifer recharge from the lake,

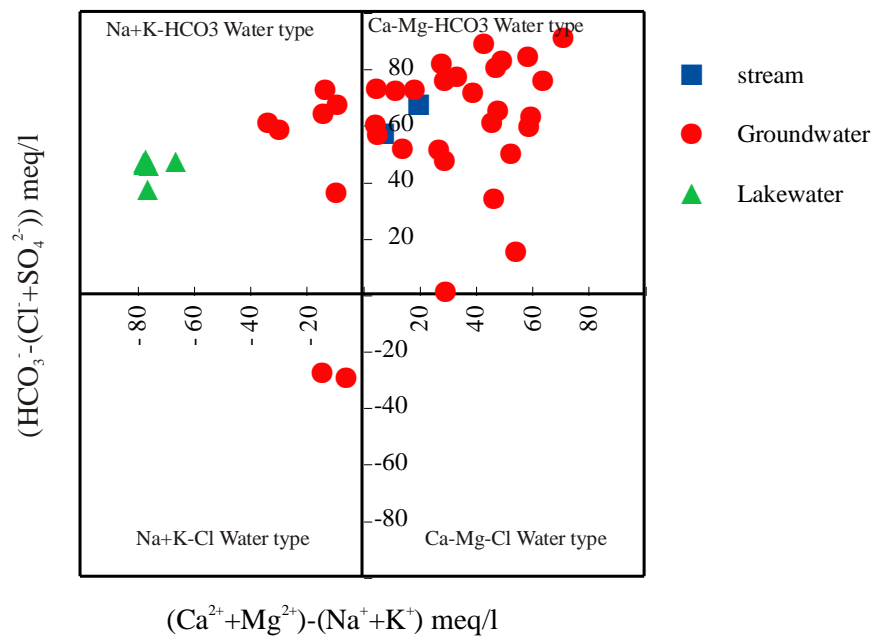


Fig. 2.3: Chadha diagram showing the hydrochemical facies of the study area

although the reverse cannot be discounted. The Gibbs diagram (Gibbs, 1970) (Fig. 2.4) was used to further highlight the evolutionary trends and the possible sources of variation in groundwater hydrochemistry in the area. The diagram is divided into regions based on contribution from atmospheric precipitation which are characterised by low to moderate TDS and high $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ weight ratio, rock dominance region; exemplified by moderate TDS and $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratio and an evaporation-crystallization region; typically in the high TDS and $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratio.

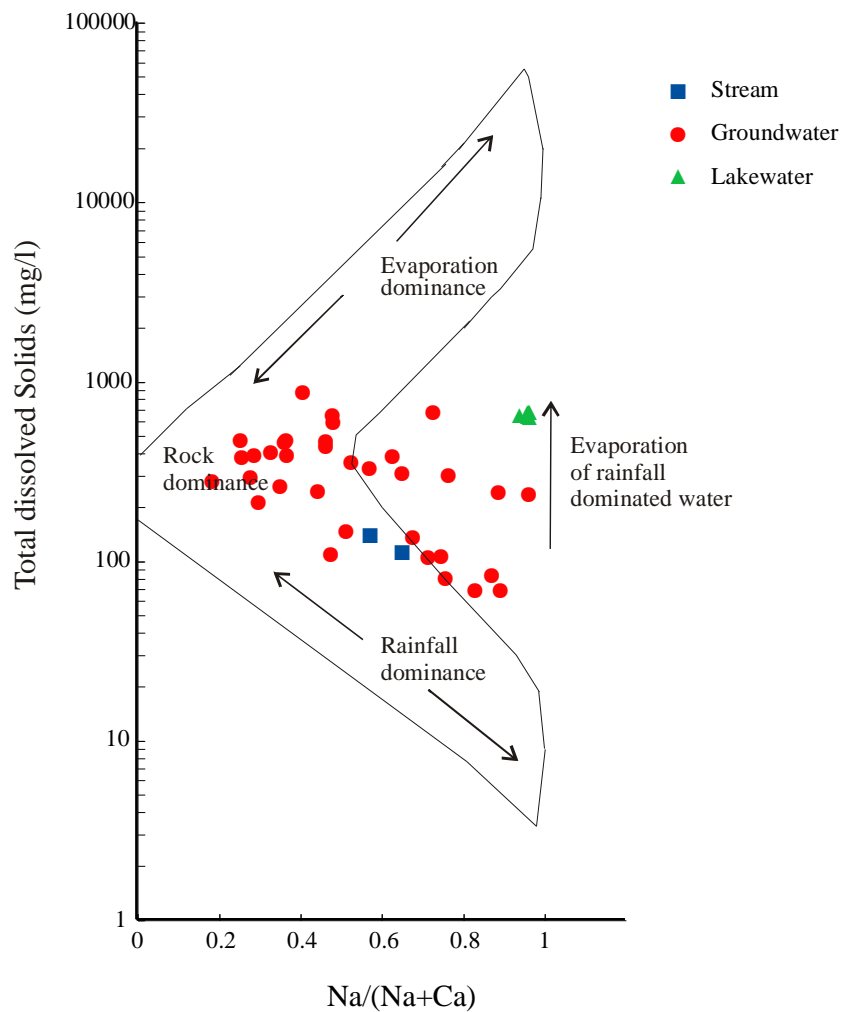


Fig. 2.4: Gibbs diagram showing the positions of the water samples in the study area.

Any other factor that influences the hydrochemistry in an aquifer apart from the three factors mentioned above cannot be identified from the Gibbs diagram. Researchers (e.g., Obiefuna and Orazulike, 2011; Yidana et al., 2012a) have used the Gibbs diagram simultaneously with other diagrams to identify the major sources of variation in hydrochemical data. For instance, Yidana et al. (2012b) used the diagram together with hierarchical cluster analysis to distinguish anthropogenic sources from the natural sources in the variation of hydrochemistry in aquifer underlying the Ankobra Basin. Similarly, Obiefuna and Orazulike (2011) effectively combined the Gibbs diagram with other geochemical distribution diagrams to identify other sources of variation that include intermixing and pollution from human activities in the hydrochemistry of waters in aquifers of the Yola area of northeast Nigeria. It is obvious (Fig. 2.4) that most of the samples in the present study plot within the rock dominance portion of the boomerang. This shows that the main mechanism influencing the hydrochemistry of the water is the interaction between the recharge water, rocks and their weathered products. These water samples are characterised by moderate TDS and $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratio. It is also obvious that the Lake water has the fingerprint of evaporative enrichment of the major parameters due to the exposure of the lake to high ambient temperatures and low humidities, which encourage surface evaporation. However, the dilution effects of inflowing rainwater (and possibly groundwater) tend to mask the effects of evaporation such that the total dissolved contents are not so high. It is also apparent that due to the obviously high residence time of much of the water in the lake, silicate mineral weathering processes have contributed significantly to the hydrochemistry of the lake. Banoeng-Yakubo (2000) asserts that weathering of the Birimian rocks have resulted in the formation of a thick regolith which constitutes the most common type of aquifer in the area. Studies on the geochemistry of soils around the crater (Boamah and Koeberl, 2002) have

indicated that rocks have reached the highest degree of weathering due to intense chemical weathering. They further stated that the soils and their parent rocks are depleted in the major ions. This probably suggests that the major ions in the groundwater may have been derived from leaching of minerals and weathering of rocks underlying the area. A few of the samples that have low to moderate TDS and high $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ ratio plot along the rainfall-rock dominance side of the diagram implying groundwater that is influenced by precipitation where the recharge process appears to be rapid and does not provide for long residence time in order for active water-rock interaction to occur. Finally, the chemistry of samples that plot outside the envelope could be influenced by evaporation of surface water and moisture in the unsaturated zone, which is influential in the development of the chemical composition of surface water bodies and shallow groundwater (Garrels and Mackenzie, 1967).

A bivariate plot of $(\text{Ca}^{2+} + \text{Mg}^{2+})$ and $(\text{SO}_4^{2-} + \text{HCO}_3^-)$ (Fig. 2.5) suggests hydrogeochemical processes that include ion exchange and the weathering of silicate and carbonate minerals as contributing to the chemistry of the groundwater. The samples that plot on the equiline ($\text{Ca}^{2+} + \text{Mg}^{2+} = \text{SO}_4^{2-} + \text{HCO}_3^-$) may indicate the weathering of carbonate and sulphate minerals that are present in the rocks of the study area. Excess $\text{SO}_4^{2-} + \text{HCO}_3^-$ ions in the samples that plot above the equiline could result from silicate mineral weathering or ion exchange processes. It is possible that the weathering of carbonates may be accounting for excess $\text{Ca}^{2+} + \text{Mg}^{2+}$ in the samples that plot below the equiline. However, silicate mineral weathering appears to be the principal hydrochemical process in the groundwater system since majority of the samples plot above the 1:1 equiline. Details on the sources of variation in the hydrochemistry of the Bosumtwi area are discussed in chapter 4.

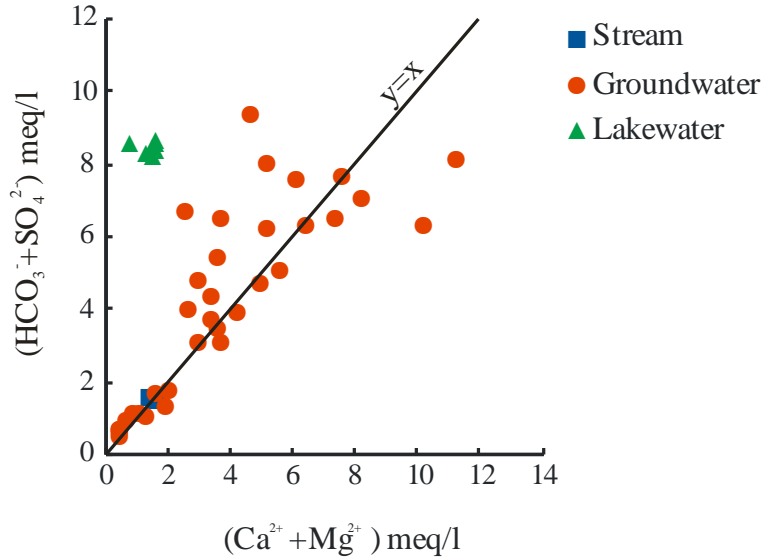


Fig. 2.5: Scatter plot of $(SO_4^{2-} + HCO_3^-)$ versus $(Ca^{2+} + Mg^{2+})$ for the samples

2.3.3 Groundwater quality assessment for domestic use

The quality of groundwater from the study area is very important because it is basically used for drinking and other domestic purposes by many individuals. Though an initial assessment of the groundwater based on parameters of health significance is made prior to its use, it is not enough. This is because, as groundwater moves along its flow path, it dissolves solutes and its chemical composition is altered with time and the quality is compromised. It is therefore imperative to continually monitor the quality of water for consumption in order to identify any changes in quality and mitigate any epidemic that may result from contaminated groundwater. It is also important to note that consumers are likely to disregard water that looks dirty/dicoloured or that has an obnoxious taste or smell to use water from sources that are aesthetically more acceptable but may not be safe. In lieu of this fact, an evaluation of the quality of the groundwater based on water quality index (WQI) has been made. The distribution of the trace elements used in

calculating WQI for the groundwater from aquifers underlying the BIC and its surrounding areas is shown in the Box plot (Fig. 2.6). The WQI provides a single value that is used to express the overall groundwater quality at a certain location and time, based on certain very important water quality parameters. This is done with the objective of turning a complex water quality data into information that is understandable by the general public and policy makers (Ramakrishnaiah et al., 2009). Parameters such as the pH, TDS, Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^- , F^- , Fe, As, Mn, Cu, Zn, Pb, Ni and Cd were considered in calculating the WQI in three steps. In the first step, each of these physical and chemical parameters was assigned a weight (w_i) based on their perceived effect on primary health with the highest weight of 5 assigned to parameters such as Pb, NO_3^- and F^- that are considered to have significant effects on water quality for drinking purposes. The weight (w_i) assigned to all other parameters used in this study are shown on Table 2.1.

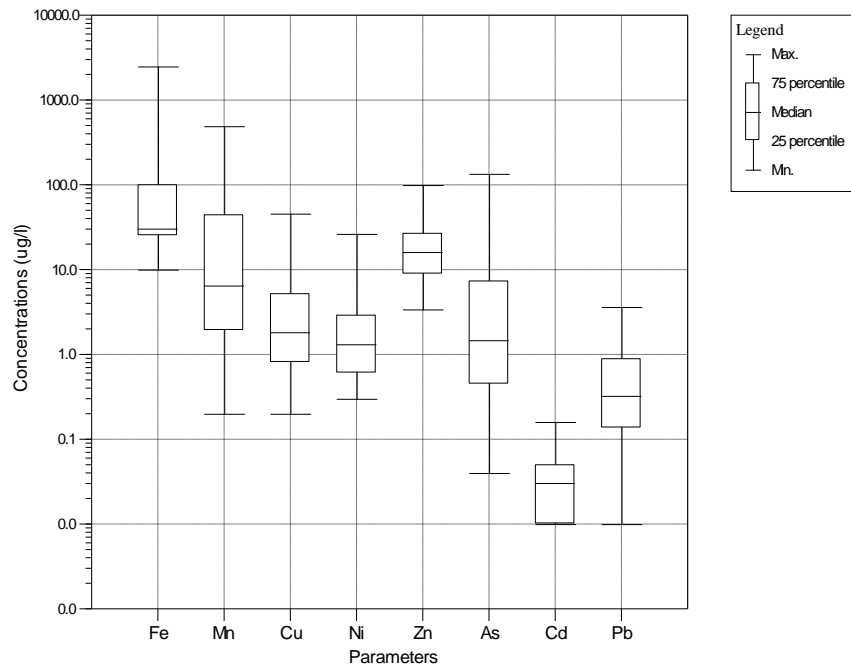


Fig. 2.6: Boxplot of trace element distribution in the groundwater samples of the study area

It is important to note that the index is subjective as it depends on the parameters chosen and their weights assigned by the researcher. In the second step, the relative weight (W_i) was computed for each parameter (equation 2.2).

$$W_i = \frac{w_i}{\sum w_i} \dots\dots\dots 2.2$$

w_i = the weight of each parameter and $\sum w_i$ = the sum of weight of all parameters.

Table 2.1 presents the w_i , W_i and WHO guideline values for each chemical parameter used in this study.

Table 2.1: WHO guideline values, weight and relative weight of each of the chemical parameters used for the WQI determination

Parameter	WHO (S_i)	Weight (w_i)	Relative weight (W_i)
pH	7.5	4	0.0741
TDS	500	4	0.0741
SO ₄ ²⁻	250	3	0.0556
Cl ⁻	250	3	0.0556
NO ₃ ⁻	50	5	0.0926
F ⁻	1.5	5	0.0926
Ca ²⁺	75	2	0.0370
Mg ²⁺	30	2	0.0370
Na ⁺	200	2	0.0370
As	0.01	4	0.0741
Cd	0.003	3	0.0556
Cu	1	2	0.0370
Fe	0.3	3	0.0556
Mn	0.1	3	0.0556
Ni	0.02	2	0.0370
Pb	0.01	5	0.0926
Zn	3	2	0.0370
		$\sum (w_i) = 54$	

The third and final step then computes a rating scale q_i , for each parameter using Equation 2.3.

$$q_i = \frac{C_i}{S_i} \times 100 \dots\dots\dots 2.3$$

C_i = the concentration of each parameter and S_i = WHO guideline value.

The water quality sub-index SI_i for each parameter is then computed (Equation 2. 4) with the overall sum (Equation 2.5) giving the WQI that reflects the composite influence of different water quality parameter.

$$SI_i = W_i \times q_i \dots\dots\dots 2.4$$

$$WQI = \sum_{n=1}^n SI_i \dots\dots\dots 2.5$$

The computed WQI values are usually classified into five categories (Table 2.2) (Sahu and Sikdar, 2008) and provides a much more global picture of the suitability of groundwater for domestic uses.

Table 2.2: Classification categories of WQI (Sahu and Sikdar, 2008)

WQI	Category
< 50	Excellent water
50–100	Good water
100–200	Poor water
200–300	Very poor water
> 300	Water unsuitable for drinking

The results based on this classification scheme for each sample presented on Table 2.3 classify all the groundwater samples as good to excellent for human consumption. All the major ions and some of the trace elements used in calculating the WQI have concentrations within the WHO (2011) guideline values for domestic use. However, six samples representing about 18% of total samples show elevated Mn above 100 µg/l, the guideline value of WHO. Two of the boreholes; GW055 and GW056 located at Adaito have manganese concentration of 492 µg/l and 267 µg/l respectively. The others include GW057 (186 µg/l), GW048 (119 µg/l), GW062 (367 µg/l) and GW069 (158 µg/l) and are, respectively located at Yapesa, Dunkura, Brodekwano No. 2 and Adumasa. The borehole located at Brodekwano No. 2 is the only borehole that has nickel concentration above the WHO guideline value. On the other hand, Fe concentration in five boreholes exceeded the WHO recommended value of 300 µg/l. These include GW042 (350 µg/l), GW048 (510 µg/l), GW056 (1020 µg/l), GW070 (730 µg/l) and GW069 (2490 µg/l). While GW070 and GW069, both located at Adumasa visibly show sediment loads in the groundwater, the others were noted as dirty during sample filtration. Even though the guideline value for both iron and manganese are for aesthetic reasons, their presence in groundwater can indicate deteriorating groundwater quality which may cause adverse health effects (Bartram and Balance, 1996; Chapman, 1996). In fact complains of food discoloration has been reported by consumers in these communities.

Table 2.3: WQI and classification of groundwater from the Study area

StationID	Sample ID	WQI	Classification	StationID	Sample ID	WQI	Classification
Esaase	GW007	23.09	Excellent	Konkoma	GW045	29.83	Excellent
Adwafo	GW012	26.76	Excellent	Brodekwano2	GW046	20.58	Excellent
Obo	GW015	17.94	Excellent	Dunkura	GW048	38.53	Excellent
Obo	GW016	15.61	Excellent	Abosoma Jyide	GW054	12.57	Excellent
Pipie Kese	GW020	27.23	Excellent	Adaito	GW055	65.20	Good
Brodekwano	GW021	45.68	Excellent	Adaito	GW056	53.27	Good
Apewu/Bansc	SW001	25.94	Excellent	Yapesa	GW057	28.93	Excellent
Timeabu	HW001	20.82	Excellent	Nyameani	GW058	11.58	Excellent
Dompa	GW024	20.70	Excellent	Sarpong Nkwanta	GW059	14.49	Excellent
Dompa	GW025	25.05	Excellent	Nkowinkwata	GW060	22.88	Excellent
Duase	GW028	26.46	Excellent	Pipie	GW061	39.52	Excellent
Ankaase	GW032	24.39	Excellent	Brodekwano2	GW062	54.18	Good
Ankaase	GW034	24.42	Excellent	Apewu/Banso	SW002	19.19	Excellent
Amakom	GW037	27.00	Excellent	Adumasa2	GW069	67.09	Good
Adjamam	GW039	29.32	Excellent	Adumasa2	GW070	28.43	Excellent
Beposo	GW041	24.33	Excellent	Gyapoadu	GW072	10.51	Excellent
Pemenase	GW042	34.53	Excellent	Deduako	GW074	33.15	Excellent
Konkoma	GW044	41.08	Excellent	Dwumakro	GW078	8.71	Excellent

2.3.4 Irrigation Water Quality

The quality of water used for irrigation is vital for the yield and quality of crops, maintenance of soil productivity, and protection of the environment. Therefore, the evaluation of the suitability of water for irrigation purposes should be based on criteria that are indicative of its potential to create soil conditions that will be detrimental to crop growth or to animal and humans that consume these crops. Criteria such as Salinity hazard, Sodium hazard/Sodicity, pH, Alkalinity, Specific ions (chloride, sulphate, boron, and nitrate) and microbial pathogens have been used to describe effects of irrigation water on crop production and soil quality (Bauder et al., 2011). An excess of Na in water especially for irrigation may be damaging to certain soil types. This, according to Kumar et al. (2006) reduces soil permeability and degrades the soil structure thereby restricting infiltration of water into and through the soil and plant roots may not have adequate water thus plant growth and productivity is compromised. In the right proportions, Ca

and Mg can serve as a buffer to the effect of sodium on the soil. The sodium adsorption ratio (SAR) measures the sodium hazard/sodicity in relation to calcium and magnesium concentrations as shown in Equation 2.6 (Fetter, 1994):

$$SAR = \frac{(Na^+)}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \dots\dots\dots 2.6;$$

all parameters are expressed in milliequivalents per liter (meq/l).

The United States Salinity Laboratory (USSL, 1954) combined the SAR with the EC to classify irrigation water. In line with the USSL (1954) scheme, a plot of SAR against EC on a semi-log axis (Fig. 2.7) was made to assess the quality of water from the study area for irrigation purposes.

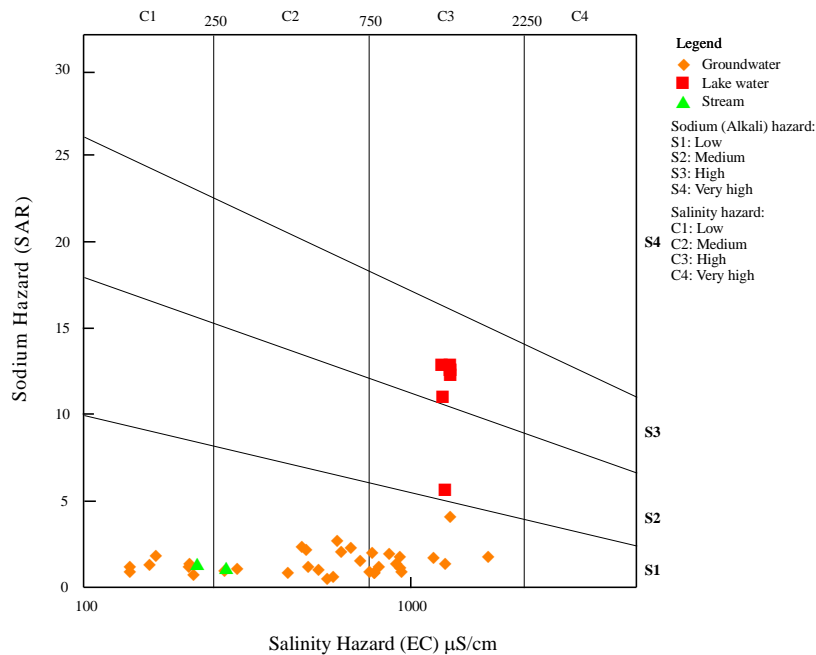


Fig. 2.7: USSL diagram of Sodium hazard (SAR) versus Salinity hazard (EC) for the samples

The diagram classifies the water into five (5) categories of low salinity/sodium hazard (C1S1), medium salinity/low sodium (C2S1), high salinity/low sodium hazard (C3S1), high salinity/medium sodium hazard (C3S2) and high salinity/high sodium hazard (C3S3) irrigation waters (Fig. 2.7). About 21% of groundwater samples that plotted within the C1S1 region of the USSL diagram are acceptable for irrigation of most crops and almost all soil types and the potential of this class of irrigation water to cause infiltration problem is improbable. The C2S1 category contains about 38% of groundwater samples. This irrigation water type can be used for the irrigation of most crops but can be detrimental to salt sensitive crops that include but not limited to beans and peanuts. Forty-one percent (41%) of the studied groundwater samples plot in the high salinity/low sodium hazard (C3S1) field. This type of irrigation water can have undesirable effect on moderately sensitive crops such as grains, forage and vegetables, and therefore, should not be applied on soils with restricted drainage (Kumar et al., 2007). The lake water plot within the C3S2 and C3S3 field and are not suitable for irrigation. However, where it becomes necessary to use the lake water for irrigation, it should be used only on salt tolerant crops and on soils that have very high permeability like sands. The use of this category of water for irrigation requires special soil and water management (Kumar et al., 2007).

Another classification scheme, Wilcox diagram, introduced by Wilcox (1955) was utilized to assess the quality of the water for irrigation activities in the area. This classification scheme measures the sodium percent (Na %) defined by:

$$Na \% = \frac{(Na^+)}{Na^+ + K^+ + Ca^{2+} + Mg^{2+}} \times 100 \dots\dots\dots 2.7;$$

all ionic concentrations are in meq/l

Like the USSL diagram, the Wilcox diagram also classifies irrigation water quality on the basis of the content of sodium. This diagram was used to substantiate the findings based on the USSL classification system. The Wilcox diagram (Fig. 2.8) shows that all but one groundwater sample fall within the ‘Excellent to good’ (68%) and ‘good to permissible’ (29%) irrigation water categories, thus classifying the groundwater as suitable for irrigation. However, the lake samples plot within the ‘doubtful to unsuitable’ category hence continued application of the lake water for irrigation over time may accumulate sodium onto soil particles and cause swelling/dispersion of soil clays, surface crusting and pore clogging. The soil eventually becomes hard and compact when dry, thereby obstructing infiltration and possibly increase surface runoff (Bauder et al., 2011). Consequently, the lake water cannot be used for irrigation, or it should be used only on salt tolerant crops and on soil types that are highly permeable and not particularly susceptible to developing sodicity related problems. The residual sodium carbonate (RSC) expressed in meq/l (equation 2.8) is an important index used to determine the HCO_3^- hazard and the suitability of water used in agriculture. The calculated RSC varied from -5.10 meq/l to 3.65 meq/l with an average -0.02 meq/l in the groundwater, while the lake water has a mean value of 7.01 meq/l.

$$RSC = \left(\text{HCO}_3^- + \text{CO}_3^{2-} \right) - \left(\text{Ca}^{2+} + \text{Mg}^{2+} \right) \dots\dots\dots 2.8$$

Classification of water quality for irrigation, according to RSC indicates that 85% of the total groundwater samples fall below RSC value of 1.25 and are, therefore, suitable for irrigation. Three other groundwater samples, representing 8% of the total number, are in the marginal range of 1.25 – 2.5, while the remaining 7% and all the lake samples have values greater than 2.5, suggesting that they are not suitable for irrigation. McLean and Jankowski (2000) stated that

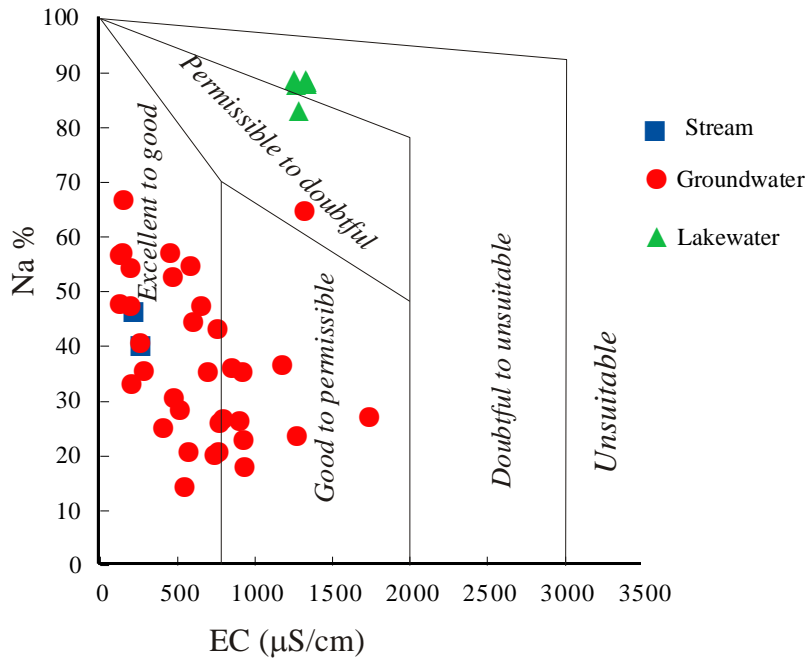


Fig. 2.8: A Wilcox diagram showing classification of irrigation water in the study area

high levels of carbonates and bicarbonates in irrigation water can lead to calcite precipitation leaving sodium as the dominant ion in solution thus decreasing soil permeability, lowering infiltration capacity and increasing erosion causing stunted plant growth. Excessive bicarbonates in the lake water can also be problematic for micro-spray irrigation systems where scale build up can clog orifices and result in reduced flow rates. On the whole, the groundwater in the area is suitable for irrigation. The lake water is not generally suitable for irrigation but can be used where necessary under careful soil and water management practices.

Conclusions

Results of the hydrochemical studies of aquifers around Lake Bosumtwi classify the groundwater as slightly acidic, moderately hard to very hard with alkaline earths (Ca + Mg) exceeding alkali (Na + K) metals. The lake water on the other hand is alkaline showing an excess of alkali metals over the alkaline earth metals. The relative ionic richness of both water bodies suggest that there is no apparent incipient relationship which benefits the main aquifer system in terms of recharge. Ca-Mg-HCO₃ hydrochemical facies dominate the groundwater while the lake water is Na-HCO₃ water type. The study also suggests that the reservoirs studied acquired their chemistry from water-rock interaction processes. WQI classify all the groundwater samples as good to excellent for human consumption. An evaluation of the suitability of both groundwater and lake water for irrigation purposes based on salinity, sodicity and residual sodium carbonate (RSC) reveal that the groundwater in the area is generally suitable for irrigation. On the whole, the lake water is not suitable for irrigation. However, where necessary, it can be used in on highly permeable soils and on salt tolerant crops under special soil and water management practices.

References

- Adu, S., Darko, E. O., Awudu, A. R., Adukpo, O. K., Emi-Reynolds, G., Obeng, M., Otoo, F., Faanu, A., Agyeman, L. A., Mensah, C.K., Hasford, F., Ali, I. D., Agyeman, B. K. and Kpordzro, R. 2011. Preliminary Study of Natural Radioactivity in the Lake Bosumtwi Basin. *Research Journal of Environmental and Earth Sciences*, 3(5), 463-468.
- Anku, Y., Banoeng-Yakubo, B., Asiedu, D. K. and Yidana, S. M., 2009. Water quality analysis of groundwater in crystalline basement rocks, Northern Ghana. *Environmental Geology*, 58(5), 989-997.
- Appelo, C. A. J. and Postma, D., 2005. *Geochemistry, groundwater and pollution*. 2nd Edition ed.: Rotterdam, A.A. Balkema.
- Banoeng-Yakubo, B. K., 2000. *The Application of Remote Sensing and Geographical Information Systems to Hydrogeological studies in the Upper West Region, Ghana*. (PhD Thesis). University of Ghana.
- Bartram, J. and Balance, R., 1996. *Water Quality Monitoring A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes*. London: E & FN Spon
- Bauder, T. A., Waskom, R.M. Sutherland, P.L. and Davis, J. G., 2011. *Irrigation water quality criteria*. Colorado State University Extension.
- Boamah, D. and Koeberl, C., 2002. Geochemistry of Soils from the Bosumtwi Impact Structure, Ghana, and Relationship to Radiometric Airborne Geophysical Data. In: Plado, J. and Pesonen, L. eds. *Impacts in Precambrian Shields*. Springer Berlin Heidelberg, 211-255.

- Boamah, D. and Koeberl, C. 2007. The Lake Bosumtwi impact structure in Ghana: A brief environmental assessment and discussion of ecotourism potential. *Meteoritics & Planetary Science*, 42(4-5), 561-567.
- Chadha 1999. A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrogeology Journal*, (7), 431–439.
- Chapman, D., 1996. *Water Quality Assessments -A Guide to Use of Biota, Sediments and Water in Environmental Monitoring* 2nd ed. London: E&FN Spon, an imprint of Chapman & Hall.
- Fetter, C. W., 1994. *Applied Hydrogeology*. 3rd ed. New York: Macmillan College Publication.
- Flusche, M. A., Seltzer, G., Rodbell, D., Siegel, D. and Samson S. 2005. Constraining water sources and hydrologic processes from the isotopic analysis of water and dissolved strontium, Lake Junin, Peru. *Journal of Hydrology*, 312(1-4), 1-13.
- Garrels, R. M. and Mackenzie, F. T. 1967. Origin of the chemical composition of some springs and lakes. In: Equilibrium concepts in natural-water chemistry. *Advances in Chemistry Series*, . *American Chemical Society*, (67), 222-242.
- Gibbs, R. J. 1970. Mechanisms Controlling World Water Chemistry. *Science*, 170, 1088-1090.
- Hirdes, W., Davis, D. W. and Eisenlohr, B. N. 1992. Reassessment of Proterozoic granitoid ages in Ghana on the bases of U/Pb zircon and monazite dating. *Precambrian Research*, 56, 89-96.

- Jones, W. B. 1985. The origin of the Bosumtwi Crater, Ghana-A historical overview. *Proceedings of the Geological Association (London)*, 96, 275-284.
- Jones, W. B., Bacon, M. and Hastings, D. A. 1981. The Lake Bosumtwi impact crater, Ghana. *Geological Society of America Bulletin*, 92(6), 342.
- Junner, N. R. 1937. The Geology of the Bosumtwi caldera and surrounding country. *Gold Coast Geological Survey Bulletin*, 8, 1-38.
- Karikari, F., Ferrière, L., Koeberl, C., Reimold, W. U., and Mader, D. 2007. Petrography, geochemistry, and alteration of country rocks from the Bosumtwi impact structure, Ghana. *Meteoritics & Planetary Science*, 42(4-5), 513-540.
- Karp, T., Milkereit, B., Janle, P., Danuor, S. K., Pohl, J., Berckhemer, H. and Scholz, C. A. 2002. Seismic investigation of the Lake Bosumtwi impact crater: preliminary results. *Planetary and Space Science*, 50, 735-743.
- Kesse, G. O., 1985. *The mineral and rock resources of Ghana*. Boston: Rotterdam, A.A. Balkema.
- Koeberl, C., Bottomley, R., Glass, B. P. and Storzer, D. 1997. Geochemistry and age of Ivory Coast tektites and microtektites. *Geochimica et Cosmochimica Acta*, 61(8), 1745-1772.
- Koeberl, C., Brandstatter, F., Glass, B. P., Hecht, L., Mader, D. and Reimold, W. U. 2007a. Uppermost impact fallback layer in the Bosumtwi crater (Ghana): Mineralogy, geochemistry, and comparison with Ivory Coast tektites. *Meteoritics & Planetary Science*, 42(4/5), 709-729.

- Koeberl, C., Milkereit, B., Overpeck, J. T., Scholz, C. A., Amoako, P. Y. O., Boamah, D. Danuor, S., Karp, T. Kueck, J., Hecky, R. E., King, J. W. and Peck, J. A. 2007b. An international and multidisciplinary drilling project into a young complex impact structure: The 2004 ICDP Bosumtwi Crater Drilling Project—An overview. *Meteoritics & Planetary Science*, 42(4/5), 483-511.
- Koeberl, C. and Reimold, W. U. 2005. Bosumtwi Impact Crater, Ghana (West Africa): An Updated and Revised Geological Map, with Explanations. *Jahrbuch der Geologischen Bundesanstalt, Wien (Yearbook of Australian Geological Survey)*, 145, 31-70.
- Koeberl, C., Reimold, W. U., Blum, J. D. and Chamberlain, P. C. 1998. Petrology and geochemistry of target rocks from the Bosumtwi impact structure, Ghana, and comparison with Ivory Coast tektites. *Geochimica et Cosmochimica Acta.*, 62(12), 2179-2196.
- Kortatsi, B. K. 2006. Hydrochemical framework of groundwater in the Ankobra Basin, Ghana. *Aquatic Geochemistry*, 13(1), 41-74.
- Kumar, M., Ramanathan, A.L., Rao, S. and Kumar, B. 2006. Identification and evaluation of hydrogeochemical processes in the groundwater environment of Delhi, India. *Environmental Geology*, 50(7), 1025-1039.
- Kumar, M., Kumari, K. Ramanathan, A. L. and Saxena, R. 2007. A comparative evaluation of groundwater suitability for irrigation and drinking purposes in two intensively cultivated districts of Punjab, India. *Environmental Geology*, 53(3), 553-574.

- Leube, A., Hirdes, W. Mauer, R. and Kesse, G. O. 1990. The early Proterozoic Birimian Supergroup of Ghana and some aspects of its associated gold mineralization. *Precambrian Research*, 46, 139-165
- Maclaren, M. 1931. Lake Bosumtwi, Ashanti. . *Geographical Journal*, 78, 270-276.
- McGregor, D. P. 1937. Results of a hydrographic survey of Lake Bosumtwi. *Gold Coast Geological Survey Bulletin*, 8, 39-46.
- McLean, W. and Jankowski, J., Groundwater quality and sustainability in an alluvial aquifer, Australia. ed. *Proceedings of the XXX IAH congress on Groundwater: Past Achievements and Future Challenges*, 26th November-1st December 2000 2000 Cape Town South Africa.
- Milovanovic, M. 2007. Water quality assessment and determination of pollution sources along the Axios/Vardar River, Southeastern Europe. *Desalination*, 213, 159-173.
- Obiefuna, G. I. and Orazulike, D. M. 2011. The Hydrochemical Characteristics and Evolution of Groundwater in Semiarid Yola Area, Northeast, Nigeria. *Research Journal of Environmental and Earth Sciences*, 3(4), 400-416.
- Prakash, S., Wieringa, P., Ros, B., Poels, E., Boateng, F. S., Gyampoh, B. A. and Asiseh, F. 2005. *Potential of ecotourism development in the Lake Bosumtwi Basin: A case study of Ankaase in the Amansie East District, Ghana*. University of Freiburg: University of Freiburg, Germany, 1616-8062.

- Ramakrishnaiah, C. R., Sadashivaiah, C. and Ranganna, G. 2009. Assessment of Water Quality Index for the Groundwater in Tumkur Taluk, Karnataka State, India. *E-Journal of Chemistry*, 6(2), 523-530.
- Rattray, R. S., 1923. *Ashanti*.
- Reimold, W. U., Brandt, D. and Koeberl, C. 1998. Detailed structural analysis of the rim of a large, complex impact crater: Bosumtwi Crater, Ghana. *Geology*, 26, 543-546.
- Rouabhia, A., Baali, F. Fehdi, Ch. Kherici, N. and Djabri, L. 2009. Hydrochemical and isotopic investigation of a sandstone aquifer groundwater in a semi arid region, El Ma El Abiod, Algeria. *Environmental Geology*, 57(8), 1699-1705.
- Sahu, P. and Sikdar, P. K. 2008. Hydrochemical framework of the aquifer in and around East Kolkata wetlands, West Bengal, India *Environmental Geology*, 55, 823-835.
- Schilling, K. E., Li, Z. and Zhang, Y.-K. 2006. Groundwater–surface water interaction in the riparian zone of an incised channel, Walnut Creek, Iowa. *Journal of Hydrology*, 327(1-2), 140-150.
- Turner, B., Gardner, L. Sharp, W. and Blood, E. 1996a. The geochemistry of Lake Bosumtwi, a hydrologically closed basin in the humid zone of tropical Ghana. *Limnology and Oceanography*, 41(7), 1415-1424.
- Turner, B. F., Gardner, L. R. and Sharp, W. E. 1996b. The hydrology of Lake Bosumtwi, a climate-sensitive lake in Ghana, West Africa. *Journal of Hydrology*, 183(3–4), 243-261.

- USSL, 1954. Diagnosis and Improvement of Saline and Alkaline Soils. *USDA Agric Handbook No. 60*. Washington DC.
- WHO, 2011. *Guidelines for Drinking-water Quality* [online]. Geneva, Switzerland.: World Health Organization. Available from: (<http://www.who.int>) [Accessed 4th March 2013 2013].
- Wilcox, L. V., 1955. Classification and use of irrigation waters. *USDA, circular 969*. Washington, DC, USA.
- Yidana, S. M., Ophori, D. and Banoeng-Yakubo, B. 2008. Hydrochemical evaluation of the voltaian system-The Afram Plains area, Ghana. *J Environ Manage*, 88, 697-707.
- Yidana, S. M., Banoeng-Yakubo, B. and Asamoah Sakyi, P. 2012a. Identifying key processes in the hydrochemistry of a basin through the combined use of factor and regression models. *Journal of Earth System Science*, 121(2), 491-507.
- Yidana, S. M., Ophori, D. Banoeng-Yakubo, B. and Samed, A. A. 2012b. A Factor Model to Explain the Hydrochemistry and Causes of Fluoride Enrichment in Groundwater from the Middle Voltaian Sedimentary Aquifers in the Northern Region, Ghana. *ARPJ Journal of Engineering and Applied Sciences*, 7(1), 50-68.

CHAPTER THREE

HYDROGEOCHEMICAL EVOLUTION AND STABLE ISOTOPE CHARACTERISTICS OF GROUNDWATER AND SURFACE WATER IN LAKE BOSUMTWI, GHANA

Abstract

Hydrochemical data and stable isotopes of $\delta^{18}\text{O}$ and δD were evaluated to understand the hydraulic relationship between groundwater and surface water in Lake Bosumtwi, identify probable recharge areas and groundwater flow in aquifers around the lake. Q-mode hierarchical cluster analyses (HCA) of the data uniquely distinguishes the lake water chemically and isotopically from the groundwater of the area, suggesting either the nonexistence of hydraulic connection between these system, or where it exists, it favours the lake to a limited extent. The study also discovered that recharge to the aquifers probably occurs on hill tops where the water is characteristically acidic with low level of mineralization, suggesting short residence time. Ionic concentration increased with deeper circulation and longer contact with host rock minerals and the groundwater evolved to more mineralized water. There are no significant isotopic variations in the groundwater, indicating that the aquifers are recharged by recent meteoric water that has undergone evaporative enrichment as the study established that the rate of evaporative loss of water that infiltrates the unsaturated zone is in the range of 45-51%. The lake water is significantly enriched, indicating severe evaporation over the open lake surface that resulted in an evaporative loss of ~82%. Estimated likely source rainwater suggests that the lake water is dominated by heavy rainfall events.

3.1 Introduction

Meteorological processes affect the stable isotopes of oxygen and hydrogen in water, and provide characteristic fingerprint that is fundamental to investigating the transformations of natural waters within the hydrologic cycle. In groundwater research, effective use of stable isotopes of oxygen and hydrogen include; studying meteoric transformations of recharge, quantifying mechanisms and areas of recharge, and identifying relationships between surface water and groundwater(Chen et al., 2006; Demlie et al., 2007; Cartwright et al., 2009; Abid et al., 2010; Owor et al., 2011). The isotopes are also used in tracing groundwater movement, estimate residence time and aquifer discharge, identifying paleowaters and studying water-rock interactions (Ojiambo et al., 2001; Chen et al., 2006; Demlie et al., 2007; Demlie et al., 2008; Cartwright et al., 2009; Abid et al., 2010). In isotope studies, a variety of techniques have been used in solving various hydrogeological problems, such as the identification of the actual mass transport of water from a surface water system, and tracing the source of pollution in groundwater systems (Dincer et al., 1978; Stichler and Moser, 1979; Butler et al., 2000). For instance, Butler et al. (2000) successfully applied the isotope ratios of $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ in Bellville (Cape Town) to trace the source of pollution in aquifers to sewerage sludge ponds. They further used both radioactive and stable isotopes to trace leakage in urban water reticulation system, locate leakage sites and estimate the extent of the leakage, and to obtain valuable information on the effect of physiography on a small-scale groundwater system. In their quest to identify the sources of groundwater in the lower Colorado River valley, Guay et al. (2006) used $\delta^{18}\text{O}$, δD and ^3H to show that local groundwater recharge was derived from precipitation. Similarly, Dogramaci et al. (2012) used stable isotopes to estimate groundwater recharge in arid and semi-arid regions, where recharge is thought to be dominated by very intense rainfall events,

whereas Gat and Gonfiantini (1981) noted that water that are recharged at different times in different locations or that follow different flow paths are often isotopically distinct. Similarly, Sukhija et al. (2005) used isotope and geochemical data to successfully identify various recharge processes operative in a fractured hard rock terrain with varying thicknesses of weathered zone and demonstrated that the groundwater flow patterns are quite complicated, involving various sources. Stable isotope studies in the Murray Basin in southeastern Australia have revealed that groundwater in the basin is entirely of meteoric origin, and that salts in this system were largely derived by evapotranspiration of rainfall with only minor halite dissolution, rock weathering (mainly feldspar dissolution) and ion exchange (Petrides et al., 2006). Environmental isotope investigation of groundwater bodies has thus become an important tool in water resources assessment and management, allowing conclusions to be drawn regarding recharge processes, location of recharge and discharge areas, aquifer continuity and turn-over time of groundwater (Fontes 1980, IAEA 1983).

Multivariate statistical techniques applied simultaneously with graphical methods to hydrochemical data (Guler et al., 2002; Helstrup et al., 2007; Yidana et al., 2008; Loh et al., 2012; Yidana et al., 2012b) have been useful in characterizing hydrochemical systems and providing clues to groundwater flow paths. For example, Q-mode hierarchical cluster analyses (HCA) applied to hydrochemical data by Yidana et al. (2012a) to determine the spatial relationship among groundwater samples from the Ankobra Basin resulted in three major spatial groundwater associations on the basis of major sources of variation in the hydrochemistry. Also, results from R-mode HCA of groundwater from the Volta Basin reflect the influence of both natural and anthropogenic factors on the groundwater chemistry (Loh et al., 2012). The

application of multivariate techniques in the interpretation of chemical and environmental isotopes data within hydrogeological context provides hydrogeologist with a powerful problem-solving tool, giving insights to geochemical pathways and processes in groundwater resources and groundwater quality studies.

Interactions between groundwater and surface water play a critical role in the functioning of riparian ecosystems, and incidences of water quality problems in local and regional aquifers are becoming well documented (Ojiambo et al., 2001; Sophocleous, 2002). For instance, Ojiambo et al. (2001) have used conservative tracers of Cl^- , $\delta^{18}\text{O}$, and δD to verify lake water seepage to underlying aquifer systems within the East African Rift zone of Kenya. In the context of sustainable river basin management, it is crucial to understand and quantify exchange processes between groundwater and surface water. The interaction between surface water in Lake Bosumtwi and the underlying aquifers has become a subject of intense interest in the recent past. This study commenced with the assumption that boreholes located within the crater rim and in close proximity to the lake receive recharge from the lake (Yidana, pers. Comm.). To further deepen our understanding of the recharge processes in the aquifers surrounding Lake Bosumtwi, this study seeks to characterize the isotopic signature of groundwater and lake water, identify plausible recharge areas and groundwater movement, and define possible geochemical evolutionary trends. Ultimately, the paper will use hydrochemical and environmental isotope data of water to investigate any possible hydraulic connection between the lake and the aquifer system surrounding the former. It is expected that the results of the study will provide clues for the understanding of groundwater recharge, flow pattern and hydrochemical processes occurring

within the Bosumtwi impact crater (BIC) and its environs. The results will be used to further establish the basic framework for future hydrological studies.

3.2 Materials and Methods

Water sampling was carried out within a relatively cool and dry period of July 20-August 5, 2012, following standard procedures. The samples were collected in 50-ml sterilized polypropylene tubes in triplicates. Two of the three sets of sampled water were filtered through a 0.45 μm cellulose acetate membrane; one of which was acidified with pure nitric acid (HNO_3^-) to $\text{pH} < 2$ for major cations and Si content analyses while the other unacidified sample was used for anion analysis. The third unfiltered sample was used to determine oxygen and deuterium isotopes. The samples were stored and transported in cushioned cooler boxes to the laboratory for analysis. The field and laboratory procedures employed for sample collection and data analyses for major and minor ions are copiously described in Chapter 2 (Section 2.2).

Three rainfall samples collected from 3 events in April, May and June, 2012 were analysed for oxygen and deuterium isotopes. These were analysed at the Department of Earth and Environmental Sciences, University of Rochester, using Los Gatos Research Liquid Water Isotope Analyzer. The results were reported in per mil (‰) relative to VSMOW (Vienna Standard Mean Ocean Water) and normalized (Coplen, 1994) on scales such that the hydrogen and oxygen isotopic values of V-SMOW were 0.0 ‰ and 0.0 ‰, respectively, while the hydrogen and oxygen isotopic values of SLAP were -428 ‰ and -55.5 ‰, respectively. The 2-sigma uncertainties of hydrogen and oxygen isotopic results were 2.0 ‰ and 0.20 ‰, respectively, unless otherwise indicated. This means that if the same sample was resubmitted for

isotopic analysis, the newly measured value would fall within the uncertainty bounds 95 percent of the time.

The Statistical Package for Social Sciences (SPSS), Microsoft Excel, and other bivariate and multivariate statistical methods were used to evaluate the dataset obtained. Multivariate statistical analyses examine the relationships among multiple variables in the whole data set and bring out the intrinsic interdependence among observations (either cases or variables) with emphasis on revealing natural groupings/clusters within the data set that would otherwise not be noticeable. The strategy used in cluster formation is agglomerative, with each observation starting as a cluster of its own and pairs of separate cluster are then combined sequentially until all clusters are joined in a complete classification tree. This brings out the structure of a data set by reducing it to a more manageable size, while retaining as much of the original information as possible. In this way, the underlying dimensions of a data set can be measured in a meaningful way (Field, 2005). Optimal multivariate statistical analysis requires that the data is normally distributed and since most naturally occurring elements are usually not normally distributed (Guler et al., 2002; Rummel, 1970) the data were log-transformed so that they more closely corresponded to normally distributed data and subsequently standardized using equation 3.1. Standardization to the z-score scales the log-transformed data to a range of roughly -3 to +3 standard deviations centered about a mean of zero. Each variable then attains an equal weight in the statistical analyses. These transformations according to Rummel (1970) do not only normalize and reduce outliers but also tend to homogenize the variance of the distribution ensuring that all parameters are close in terms of their variances. Otherwise the Euclidean

distances will be influenced most strongly by the variable that has the greatest magnitude (Judd, 1980; Berry, 1995).

$$z = \frac{x - \bar{x}}{s} \dots\dots\dots 3.1$$

x , \bar{x} and s are respectively the data, the mean and the standard deviation.

In this study, Q-mode hierarchical cluster analyses (HCA) which classifies samples was applied to the standard z-scores using the statistical software package SPSS 20 for windows (Corp, 2011). HCA was applied with the aim of grouping the samples into clusters based on similarities or dissimilarities within the dataset. These clusters are then progressively (hierarchically) merged or linked to produce a dendrogram. Though several methods exist for distance measure and linkage, Euclidean distance and squared Euclidean distance measure calculated from equations 3.2 and 3.3 for similarity measurement and the Ward’s criterion for linkage are widely utilized in hydrochemical studies. Guler et al. (2002) explained that the combined use of the squared Euclidean distance and Ward’s criterion produces the most distinctive groups where each member within a group is more similar to its fellow members than any other member from outside the group.

$$d_{ab} = \sqrt{\sum_{i=1}^j (a_i - b_i)^2} \dots\dots\dots 3.2$$

$$d_{ab}^2 = \sum_{i=1}^j (a_i - b_i)^2 \dots\dots\dots 3.3$$

Where d_{ab} = Euclidean distance between two points a and b in space and i defines each parameter.

3.3 Results and Discussions

3.3.1 Major ion chemistry

The physical and chemical data of groundwater and lake water obtained in this study are summarized in Fig. 3.1. Average temperatures recorded for groundwater and lake water during sampling were around 27°C. The Total Dissolved Solids (TDS) vary from 69 to 873 mg/L with a mean of 332.03 mg/l for the groundwater and an average TDS value of ~658 mg/L was recorded for the lake water with minimum and maximum values of 634 and 627 respectively.

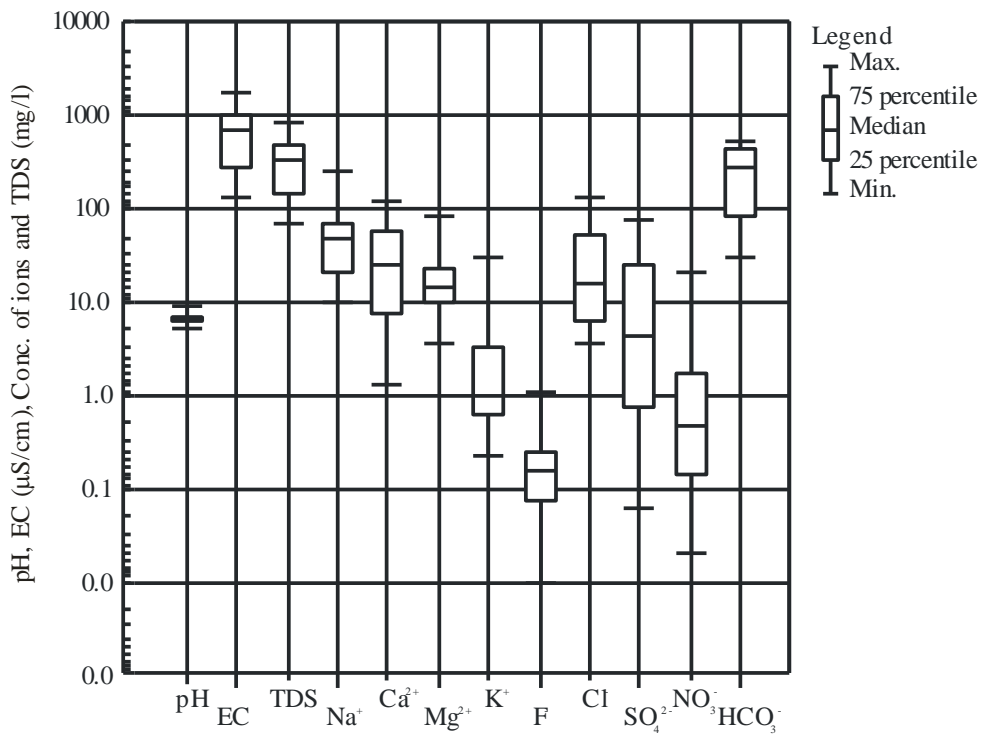


Fig. 3.1: Box plot for the physical and major ions for the water samples from the study area

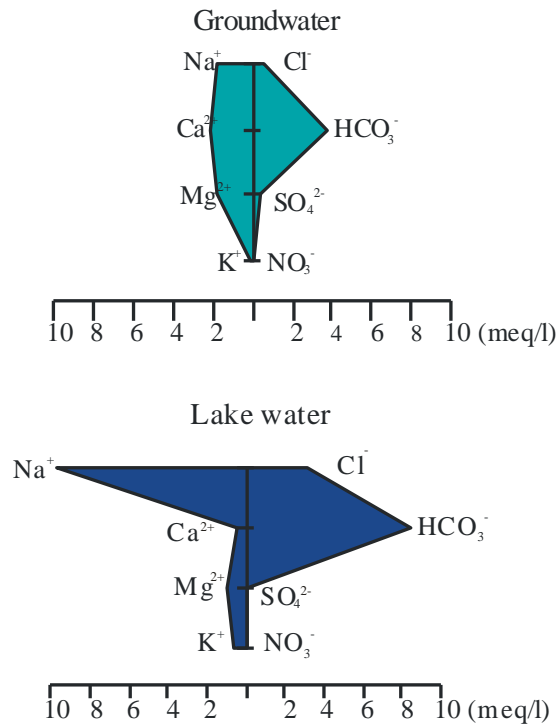


Fig. 3.2: Stiff diagrams for the mean concentration of the major ions in groundwater and lake water.

The concentration distribution of the various major ions in the groundwater are indicated on the box plot (Fig. 3.1) and shows that the hydrochemistry is dominated by bicarbonates, calcium, magnesium and sodium ions. The average cation concentrations observed in the groundwater occur in the order of $Ca \geq Mg \approx Na \gg K$, while in the lake water the trend is generally $Na \gg Mg > K > Ca$. In both systems however, average anion concentrations are in the order of $HCO_3^- > Cl^- \approx SO_4^{2-} \gg NO_3^-$ for GW and $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ for LW (Fig. 3.2).

Q-mode HCA performed on the physico-chemical parameters of the samples to examine the probable spatial variation in the hydro-geochemical properties produced four clusters (Fig. 3.3).

These clusters are ordered from right to left with respect to increasing EC and pH. Figures 3.4 and 3.5 depict the spatial distribution of EC and pH and their relationship with the clusters. Clusters 1 to 3 are exclusively groundwater samples that generally show evolutionary trends from higher (on top of the crater rim) to lower (within the crater rim) elevations while the lake water samples are grouped in cluster 4 (C4).

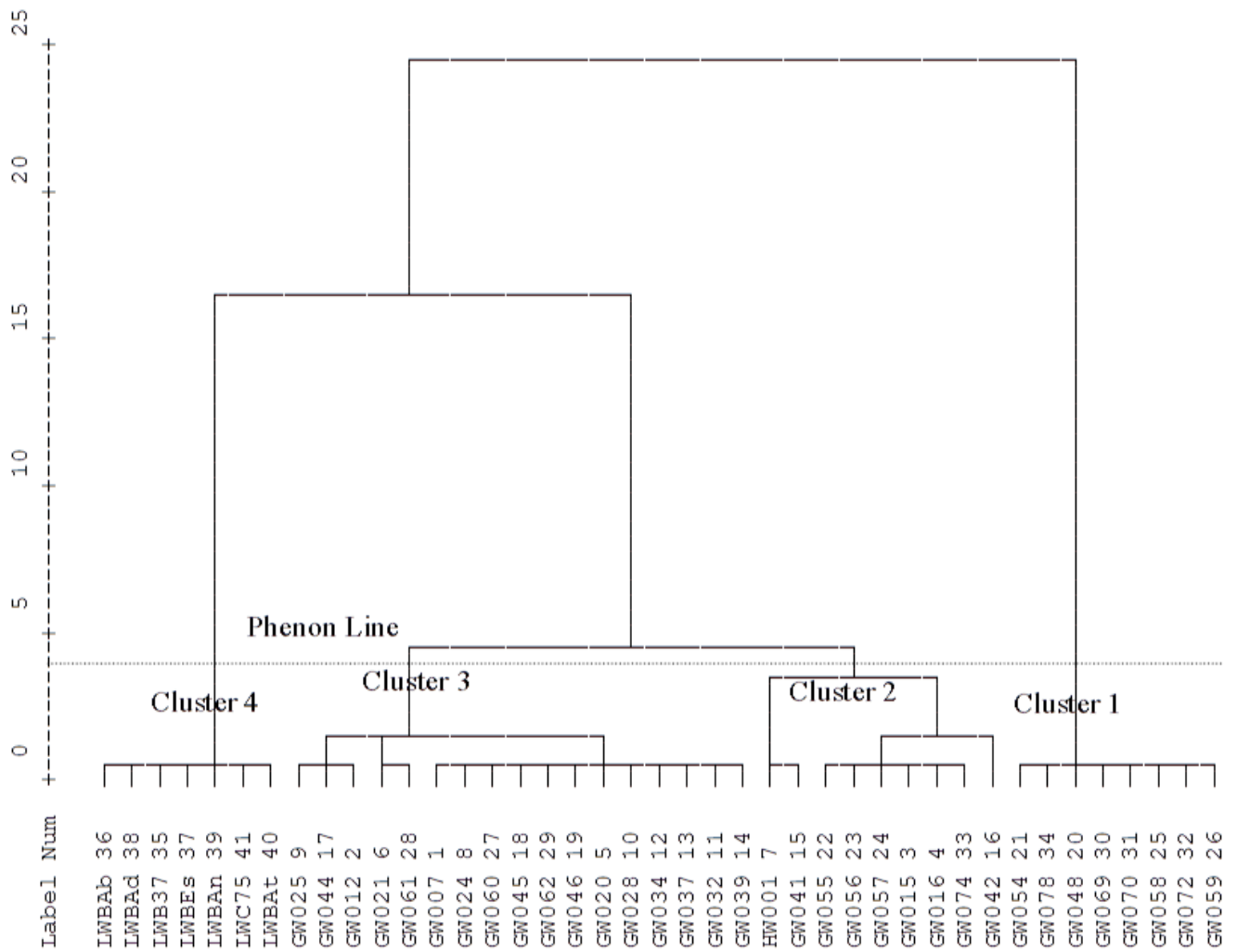


Fig. 3.3: Dendrogram generated from HCA of hydrochemical data from groundwater and lake water showing associations between the samples

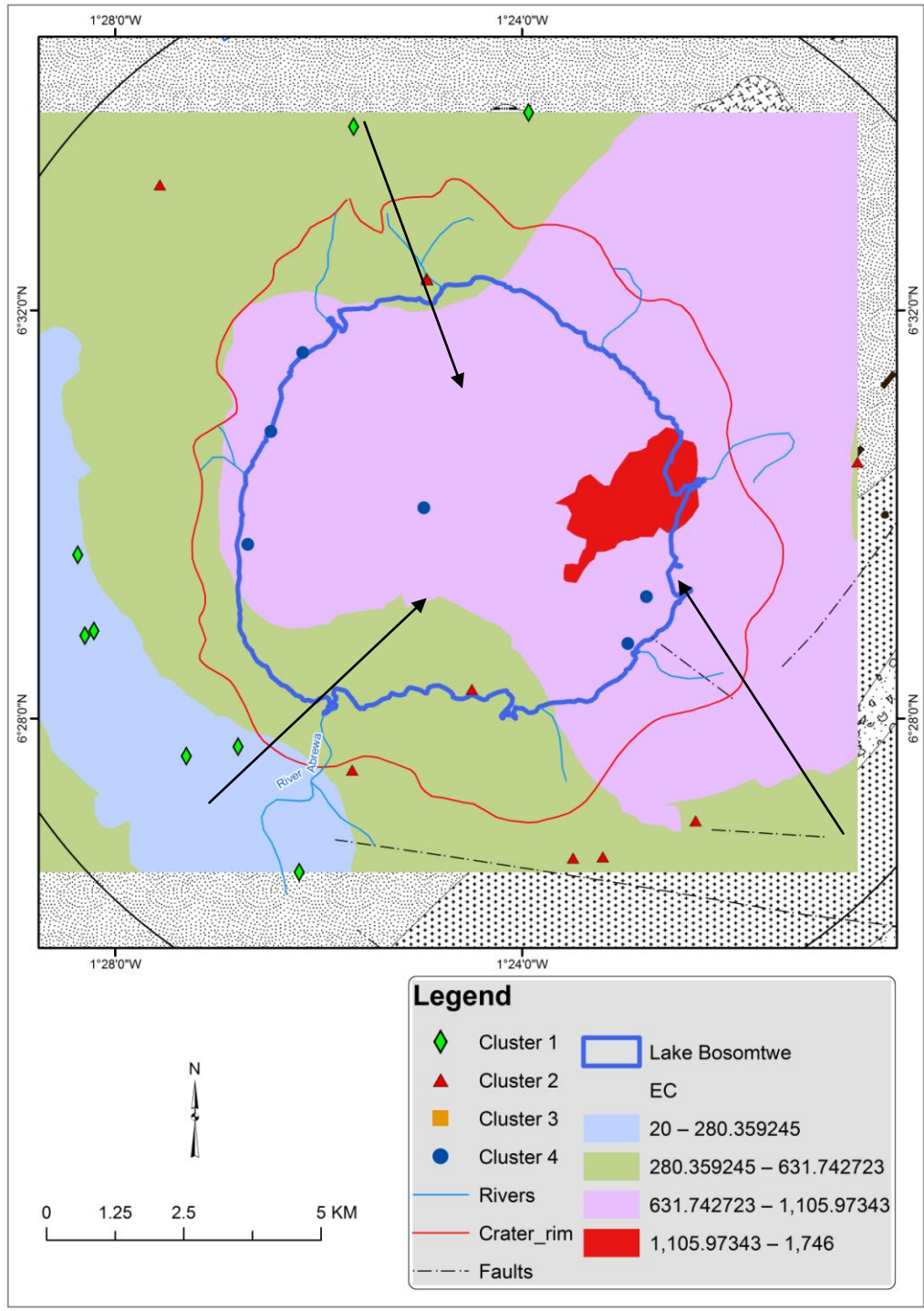


Fig. 3.4: Spatial distribution of EC ($\mu\text{S}/\text{cm}$) in relation to sample clusters. Arrows show direction of increasing EC

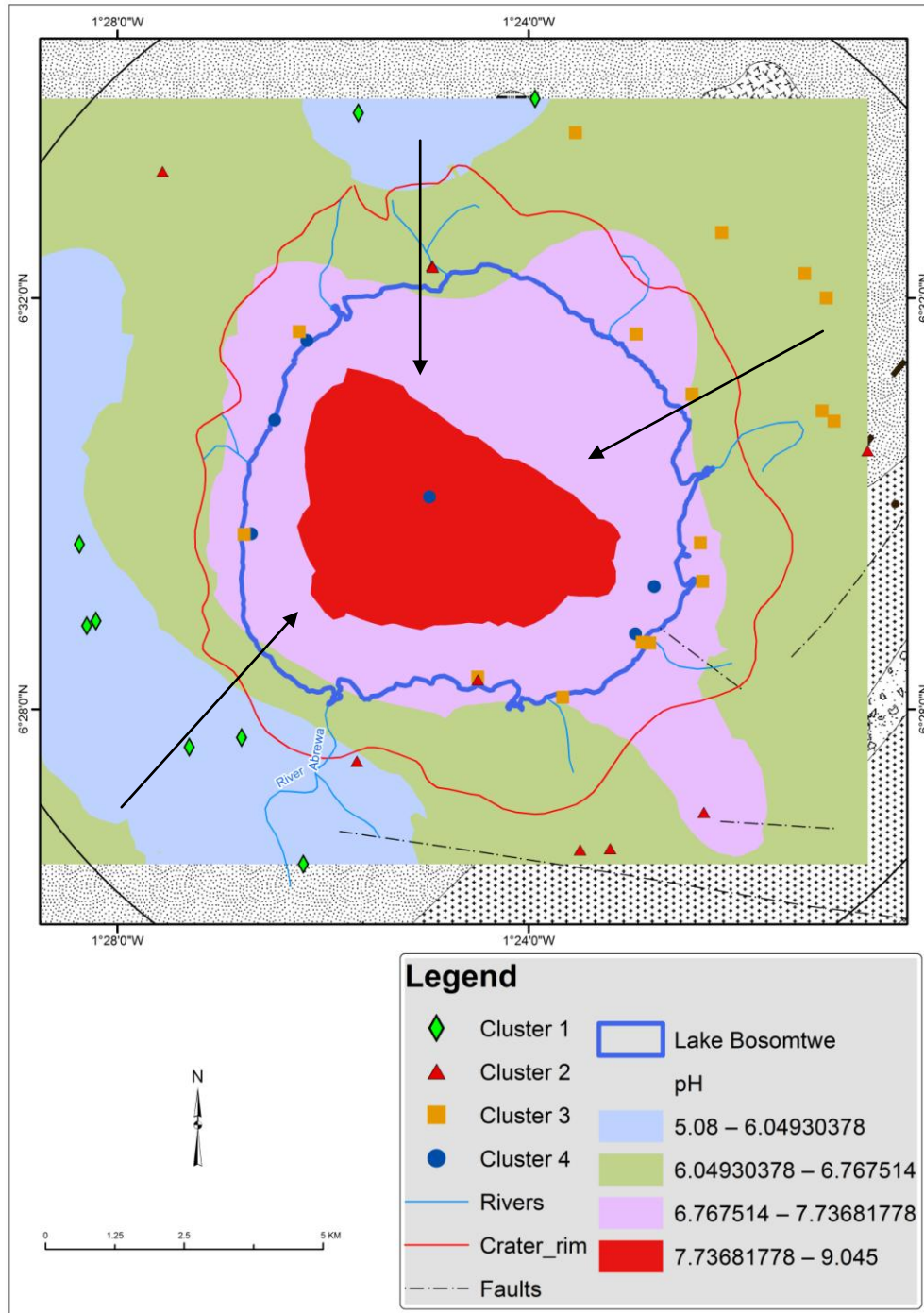


Fig. 3.5: Spatial distribution of pH (pH units) in relation to sample clusters. Arrows show direction of increasing pH

Cluster 1 (C1) samples are acidic (median pH = 5.61) and weakly mineralized (median EC = 188 $\mu\text{S/cm}$; Table 3.1) and are generally located SW on the fringes of the crater rim at an average elevation of 308 m asl (Figs. 3.4 and 3.5).

The low pH observed in C1 waters probably resulted from the dissolution of atmospheric CO_2 in recharging rain water and a subsequent dissolution of CO_2 from plant and animal respiration within the soil zone (Hem, 1989). This acidic condition created an enabling environment for silicate mineral weathering hence the higher concentration of silica observed in these waters as compared to samples of other clusters.

Table 3.1: Statistical summary of the physico-chemical parameters of the clusters.

Cluster 1																	
	Elevation (m)		pH	T (°C)	EC ($\mu\text{S/cm}$)	TDS (mg/l)	K ⁺ (mg/l)	Na ⁺ (mg/l)	Mg ²⁺ (mg/l)	Ca ²⁺ (mg/l)	Sr ²⁺ (mg/l)	Si (mg/l)	F (mg/l)	Cl (mg/l)	NO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)
Min	259	5.08	25.04	138	69	0.23	9.64	3.49	1.3	0.07	23.8	0.01	3.53	0.15	0.13	31	
Max	358	5.73	26.03	270	135	4.80	18.80	11.70	11.60	0.17	52.00	0.26	6.16	3.13	1.98	70	
Mean	307.75	5.51	25.48	189	95	1.05	15.07	5.74	4.95	0.12	36.14	0.10	4.47	0.87	0.90	51.75	
Std. Dev	27.88	0.26	0.36	46.14	23.10	1.53	3.35	2.68	3.44	0.03	9.50	0.10	0.82	1.02	0.74	15.62	
Median	306	5.61	25.39	188.00	94.00	0.57	15.75	4.81	4.60	0.12	35.20	0.08	4.15	0.54	0.61	51	
Cluster 2																	
	Elevation (m)		pH	T (°C)	EC ($\mu\text{S/cm}$)	TDS (mg/l)	K ⁺ (mg/l)	Na ⁺ (mg/l)	Mg ²⁺ (mg/l)	Ca ²⁺ (mg/l)	Sr ²⁺ (mg/l)	Si (mg/l)	F (mg/l)	Cl (mg/l)	NO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)
Min	111	5.54	24.55	295	147	0.28	17.2	7.97	1.6	0.178	13.9	0.02	4.3	0.02	0.06	57	
Max	448	7.29	28.23	662	331	4.40	67.20	23.80	69.90	0.52	38.40	1.11	60.10	13.50	22.50	290.00	
Mean	251.3	6.43	26.48	510.20	255.40	1.28	37.75	16.23	34.45	0.32	25.74	0.23	20.17	3.04	9.71	183.20	
Std. Dev	120.96	0.55	1.31	105.08	52.70	1.26	17.87	4.86	20.88	0.13	6.47	0.32	21.89	5.42	8.57	87.46	
Median	253	6.56	26.19	507.00	254.00	0.87	33.70	16.05	38.75	0.33	26.55	0.14	7.73	0.62	10.02	198.50	
Cluster 3																	
	Elevation (m)		pH	T (°C)	EC ($\mu\text{S/cm}$)	TDS (mg/l)	K ⁺ (mg/l)	Na ⁺ (mg/l)	Mg ²⁺ (mg/l)	Ca ²⁺ (mg/l)	Sr ²⁺ (mg/l)	Si (mg/l)	F (mg/l)	Cl (mg/l)	NO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)
Min	108	6.2	25.46	599	300	0.44	26.7	9.9	18.8	0.2	8.1	0.02	8.63	0.02	17.9	182	
Max	244	7.04	29.18	1746	873	4.98	105.00	84.00	120.00	0.86	22.40	0.38	69.60	21.30	79.30	494.00	
Mean	163.25	6.70	27.43	959	480	1.46	59.03	31.52	65.91	0.42	16.68	0.15	31.44	4.17	36.27	353.75	
Std. Dev	57.51	0.23	1.18	293.26	146.68	1.24	21.92	18.70	28.21	0.21	3.95	0.11	19.54	6.14	17.54	93.21	
Median	128.5	6.73	27.57	888.50	444.00	0.97	60.60	24.10	65.20	0.36	17.00	0.14	26.55	1.80	28.60	361.00	
Cluster 4																	
	Elevation (m)		pH	T (°C)	EC ($\mu\text{S/cm}$)	TDS (mg/l)	K ⁺ (mg/l)	Na ⁺ (mg/l)	Mg ²⁺ (mg/l)	Ca ²⁺ (mg/l)	Sr ²⁺ (mg/l)	Si (mg/l)	F (mg/l)	Cl (mg/l)	NO ₃ ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	HCO ₃ ⁻ (mg/l)
Min	103	8.39	26.59	1262	634	11.9	80.8	6.79	4.5	0.105	4.6	0.18	107	0.04	0.6	500	
Max	112	9.06	27.50	1344.00	672.00	28.80	260.00	14.30	9.20	0.20	11.60	0.41	138.00	0.32	0.90	526.00	
Mean	107.43	8.87	27.24	1313.29	657.57	25.04	224.97	12.63	7.73	0.19	9.94	0.26	112.00	0.13	0.76	514.43	
Std. Dev	3.36	0.23	0.34	36.20	17.21	6.29	66.31	2.72	1.52	0.04	2.60	0.07	11.47	0.11	0.12	9.69	
Median	109	8.95	27.41	1337.00	669.00	28.10	257.00	14.00	8.00	0.20	11.20	0.24	108.00	0.08	0.78	516.00	

Such process results in the release of cations, particularly Na^+ , into solution and kaolinite, a product of incongruent weathering, is formed from mainly plagioclase, biotite and K-feldspar (Garrels and Mackenzie, 1967). The low mineralization most likely suggests short residence time and rapidly recharged waters. A Schoeller diagram (Fig. 3.6), produced for the arithmetic mean of major ions reinforced the evolutionary trend observed above. The diagram (Fig. 3.6) shows that Na^+ is relatively higher than Mg^{2+} and Ca^{2+} for C1 waters. Under conditions of low pH and high CO_2 , groundwater gains much of its silica content over relatively short distance of travel resulting in a Si to Na ratio of 2:1 in the groundwater where there is dissolution of plagioclase (Garrels and Mackenzie, 1967). This is consistent with C1 water, suggesting that the groundwater in the area gained much of its Si content over a relatively short distance of travel in the presence of CO_2 -charged meteoric recharging waters that dissolve plagioclase (particularly albite) in the rocks of the study area. It is for this reason that the observed Na^+ content is high in C1 samples. Cluster 1 samples are most likely groundwater collected from shallower boreholes, probably signifying recharge areas. Moving down gradient towards respective average elevations of 251 m asl for C2 samples and 163 m asl for C3 samples in the NE (Figs. 3.4 and 3.5) ionic content increased and the water evolved from C2 waters, characterized by slight acidity (median pH = 6.55), and moderately mineralized (median EC = 507 $\mu\text{S}/\text{cm}$) to a more mineralized C3 waters having median pH and EC values of 6.72 and 888.5 $\mu\text{S}/\text{cm}$ respectively (Table 3.1 and Figs. 3.4 and 3.5). This is reflective of longer residence/contact time and increased interaction with aquifer materials (Freeze and Cherry, 1979; Stuyfzand, 1999; Appelo and Postma, 2005). No one cation dominates the samples in clusters 2 and 3; however calcium seems to be the most abundant in majority of the samples in these clusters. Various workers have used major ion

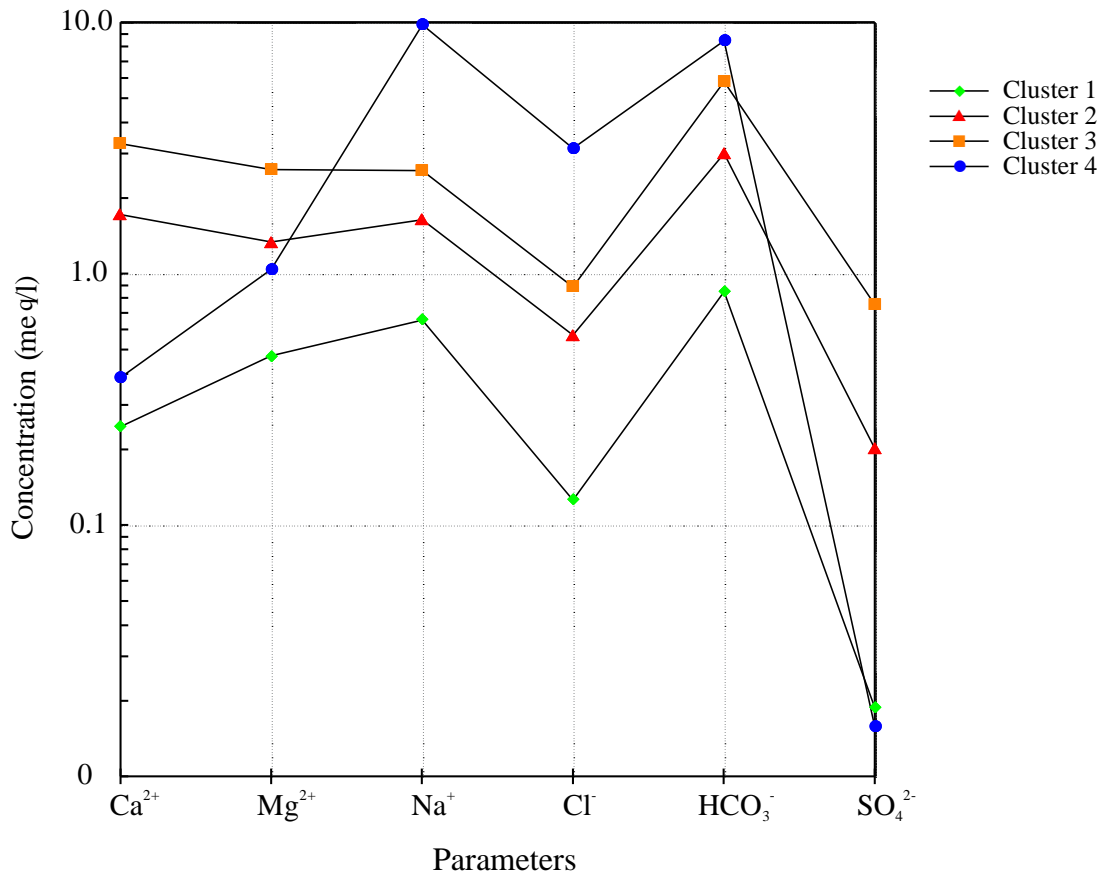


Fig. 3.6: Schoeller diagram showing the arithmetic mean of the major ions in each cluster

chemistry of groundwater in the determination of solute sources and better description and understanding of groundwater evolution (Edmunds et al., 1982; Hendry and Schwartz, 1990; Herczeg et al., 1993; Hiscock et al., 1996), while others have shown that the study of regional hydrogeochemistry is valuable to the management of regional aquifers, tracing flow and salinisation of groundwater (Panno et al., 1994; Gosselin et al., 2001; Stimson et al., 2001). It can be seen from Table 3.1 that median Si content decreases along flow path (i.e. C1 > C2 > C3), indicating the possible formation of some secondary mineral other than kaolinite that removed silica from the groundwater (Garrels and Mackenzie, 1967). Guler et al. (2002) noted that

various factors such as composition of recharge water, aquifer mineralogy and characteristics, climate and topography that influence the chemical composition of groundwater, combine to create diverse water types that change spatially and temporally. These spatial changes in the water types can be evaluated and used to trace the recharge source(s) to the groundwater system. It can then be concluded that the pattern observed is cogent with the expectation that increased rock-water interactions will result in a corresponding increase in total ionic content along groundwater flow paths.

3.3.2 *Stable Isotopes*

Evaporation is the dominant process by which natural waters undergo isotopic fractionation (Clark and Fritz, 1997). The fractionation of stable isotope of oxygen and hydrogen follows a Rayleigh distillation on a global scale, producing a linear relationship between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ for meteoric waters, where values generally plot along a trend known as the global meteoric water line (GMWL) following Equation 3.4 (Craig, 1961);

$$\delta^2\text{H} = 8\delta^{18}\text{O} + 10 \dots\dots\dots 3.4$$

The slope of the GMWL is related to the ratio of the equilibrium fractionation factors of ^2H and ^{18}O during evaporation or condensation of water (Clark and Fritz, 1997; Faure, 1998). According to Dansgaard (1964), the intercept of GMWL represents the deuterium excess (d-excess) that cannot be accounted for by the equilibrium fraction between water and vapour for the slope of 8 (Eq. 3.5).

$$d = \delta^2\text{H} - 8\delta^{18}\text{O} \dots\dots\dots 3.5$$

The d-excess (d) is strongly controlled by the relative humidity through non-equilibrium (Kinetic) evaporation process involved in the formation of water vapour and averages about 10‰ at relative humidity of ~85% on global scale (Clark and Fritz, 1997; Deshpande et al., 2003). The slope and intercept (d-excess) are useful in deciphering secondary processes that may be influencing atmospheric vapour content during evaporation and condensation (Deshpande et al., 2003; Marfia et al., 2004; Gupta et al., 2005).

Results of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotope composition for groundwater (GW), rainwater (RW) and lake water (LW) from the study area are presented on Fig. 3.7. The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for the groundwater samples varied from -3.6 ‰ to -2.3 ‰ and -16.5 ‰ to -7.6 ‰ respectively. Considering the limited data for RW and LW, the mean $\delta^{18}\text{O}$ values for the RW, GW and LW collected from the area were -4.16 ‰, -3.06 ‰ and 4.74 ‰ respectively, while those for $\delta^2\text{H}$ were -21.81 ‰, -12.46 ‰ and 23.98 ‰ respectively. Since precipitation is generally considered to be the main source of recharge to natural water bodies, it is expected that the meteoric ^{18}O - ^2H signature of the rainwater will be transferred to the groundwater and lake water in the study area. However, comparing the mean $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of the GW and LW to that of RW, a progressive enrichment is observed in their isotope compositions. The variations in the isotopic compositions of the groundwater and lake water from that of the rainwater may be an indication of some modification of the initial isotopic composition of rainwater (Clark and Fritz, 1997).

A plot of $\delta^2\text{H}$ against $\delta^{18}\text{O}$ of the analysed samples is shown on Fig. 3.8. With the limited isotopic data on rainfall from the study area, it can be seen that RW04 sampled in April is isotopically enriched and similar to the isotope content of the groundwater, compared to the events of May (RW05) and June (RW06) (Fig. 3.8). The enrichment may be attributed to amount

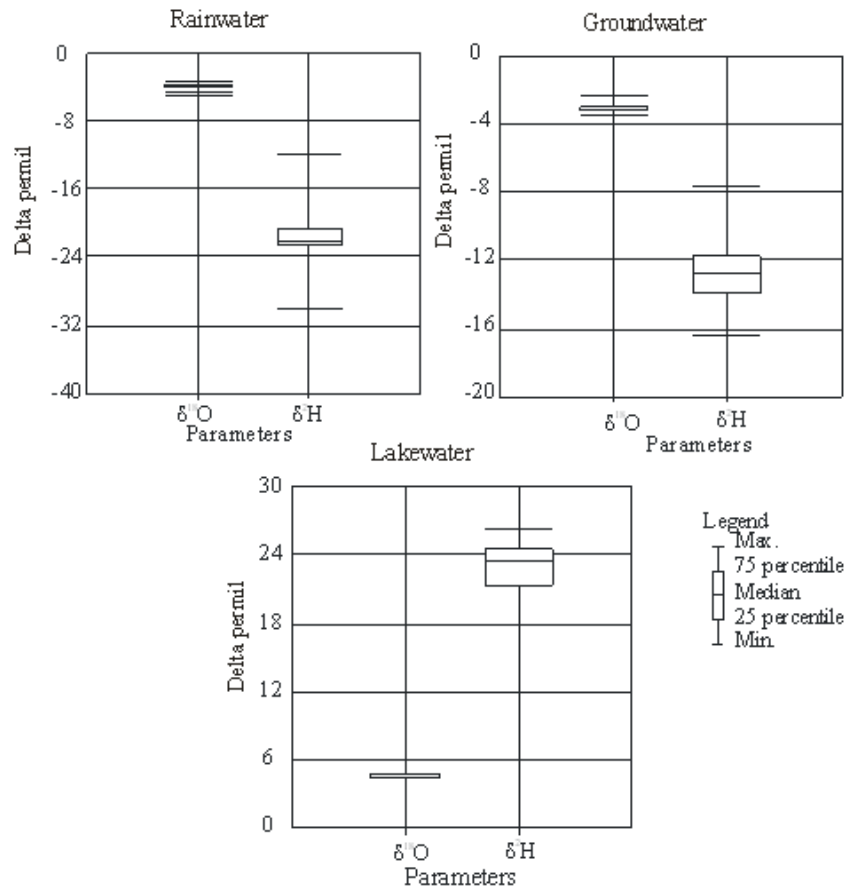


Fig. 3.7: Box plot of the stable isotope contents of the analyzed water samples.

effect (Dansgaard, 1964) as this rainfall event was an early and light one that started the major rainfall season. Such evaporative enrichment is minimized once the dry air column above the ground becomes water-saturated and subsequent rainfall events (e.g. RW05 and RW06; Fig. 3.8) become isotopically depleted (Clark and Fritz, 1997). The global meteoric water line (GMWL) provides a convenient reference line for understanding and tracing the origins and movements of water in the environment. It is good practice to establish a local meteoric water line (LMWL) from samples of individual rain events or monthly means of precipitation and compare with

surface water and groundwater data in any regional or local hydrological investigations. In this way, a better judgment on the origin and movement of groundwater and surface water in each locality can be made. Unfortunately there are no weather stations, hence no data on the isotopic composition of precipitation in the study area. However data on isotopic composition of precipitation covering 2005 and 2009, at Pwalugu (10.584444 N and 0.840833 W), located at an altitude of 140 m asl in the Upper East Region of Ghana (GNIP/WISER IAEA, 2012) have been used to draw a regression line of $\delta^2\text{H}$ against $\delta^{18}\text{O}$ for the precipitation. Using Equation 3.6, the resultant LMWL is shown in Fig. 3.8.

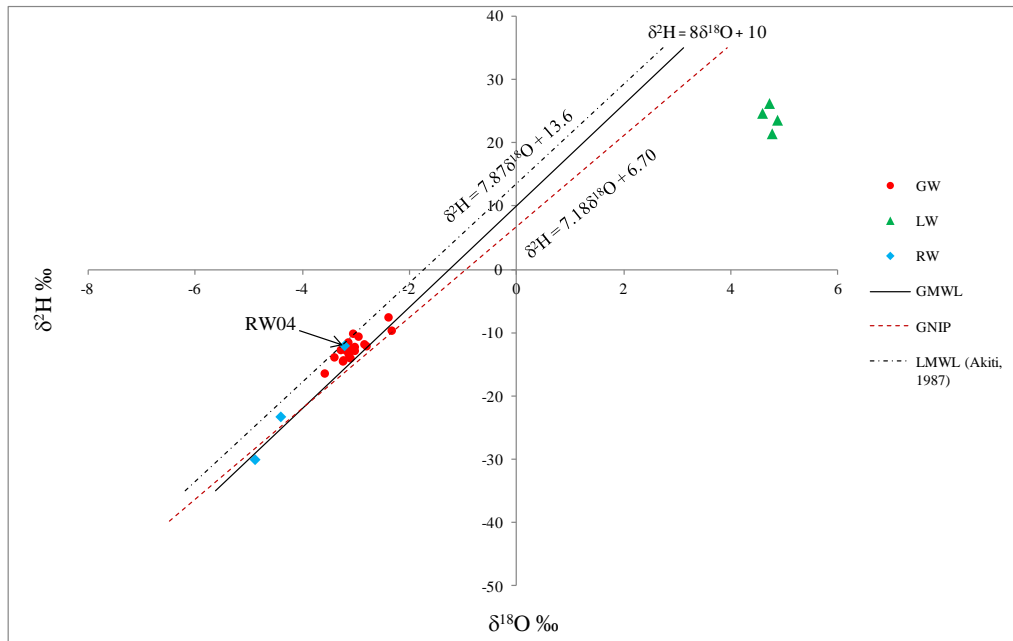


Fig. 3.8: A scatter diagram of $\delta^2\text{H} - \delta^{18}\text{O}$ of the samples analyzed in this study. Also shown are the GWML and LWML.

$$\delta^2\text{H} = 7.18\delta^{18}\text{O} + 6.70 \dots\dots\dots 3.6$$

Another LMWL, established by (Akiti, 1987) for the Accra Plains of SE Ghana (Equation 3.7) has also been shown in Figs. 3.8 and 3.9. Hoefs (2009) stated that both slope and intercept (d-excess) of LMWLs may vary depending on the prevailing local climatic and geographic conditions.

$$\delta^2H = 7.87\delta^{18}O + 13.6 \dots\dots\dots 3.7$$

In the present study, the slope and intercept of the LMWL (Equation. 3.6) described for the Upper East Region of Ghana, are lower than those established by Akiti (1987), indicative of precipitation that occurred in a warmer/dryer climate (characteristic of the Upper East Region) where significant amount of rainfall evaporate below the cloud base before reaching the ground. Clark and Fritz (1997) also noted that evaporation during rainfall will impart a kinetic fractionation on the raindrop, consequently producing lower slope and intercept (d-excess) compared to that of the GMWL. The higher d-excess observed for the LMWL established by Akiti (1987) could possibly indicate the process where momentous re-evaporation of local surface waters under low humidities (usually < ~85 %) creates vapour masses with higher d-excess (Clark and Fritz, 1997; Marfia et al., 2004; Dogramaci et al., 2012). Since the area of his study is close to the sea, it is possible that admixture of secondary moisture flux from the surface of the sea and atmospheric moisture could occur, thereby influencing the d-excess value. The relationships between δ^2H and $\delta^{18}O$ of the analyzed samples in this study are shown with the meteoric water lines MWLs (i.e. GMWL and the two LMWLs) in Fig. 3.8. Most of the groundwater (GW) and rain water (RW) samples plot between the LMWL (established by Akiti, 1987) on one hand and the GMWL and LMWL GNIP/IAEA data) on the other, with the

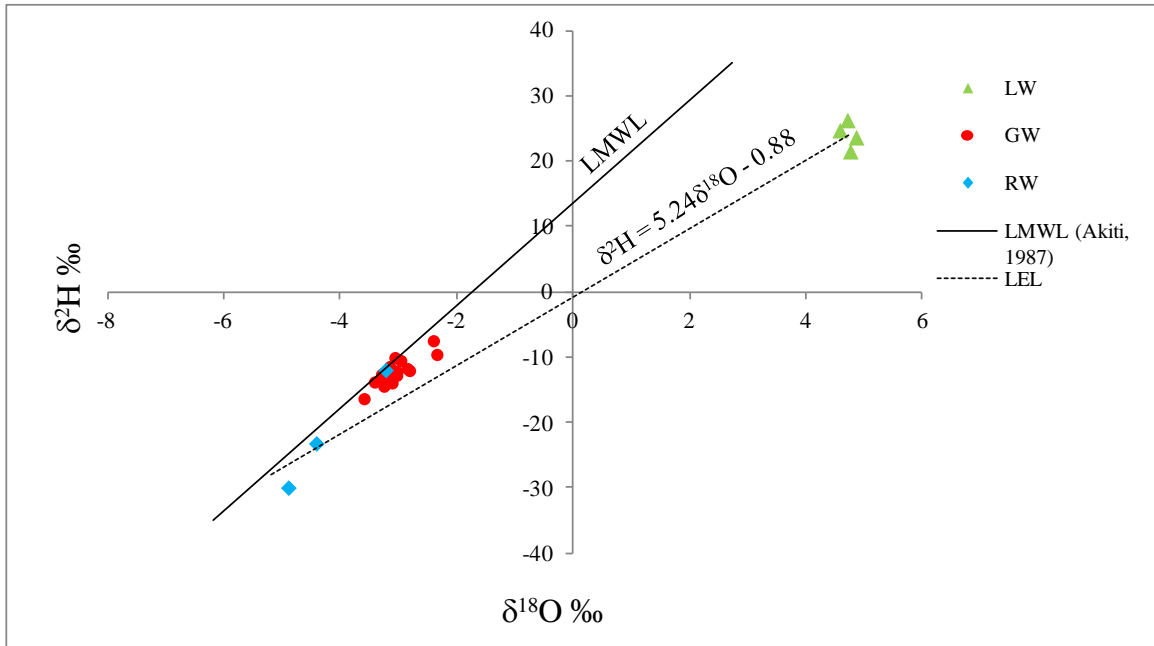


Fig. 3.9: A scatter diagram of $\delta^2\text{H} - \delta^{18}\text{O}$ of the samples along with the LEL.

remaining few falling on the MWLs. (However, the lake water (LW) samples are displaced and fall sub-parallel to the MWLs (Fig. 3.8). Meteoric waters that do not undergo or are slightly modified by evaporative enrichment usually plot on or closely to MWLs, whereas waters that are modified directly by evaporation or mixed with evaporatively enriched waters fall to the right of the MWLs (Coplen, 1993; Mazor, 1997). Thus, the GW samples that plot on or closely around the MWLs show little or no evidence of evaporation effects. The displacement of the lake water samples from the MWLs suggests evaporation occurring over the open lake surface and subsequently enriching the residual lake in the heavy isotopes (^2H and ^{18}O). Clark and Fritz (1997) noted that displacements from MWLs usually result in evaporation/mixing line with lower slopes that depend on the relative humidity. It can be seen from Fig. 3.9 that the isotopic

compositions of the lake water plot along a lake evaporation line (LEL) described by the following expression:

$$\delta^2H = 5.24\delta^{18}O - 0.88 \dots\dots\dots 3.8$$

Studies have shown that evaporative enrichments that produce lines with slopes as low as 5.2 ‰, accompanied by low d-excess, occur at relative humidity of ~75% (Clark and Fritz, 1997), which is well within the humidity range of 70-85% in the study area (Turner et al., 1996b) and produce vapour fluxes that mix with atmospheric vapour. Deshpande et al. (2003) noted that if such secondary vapour flux mixes with atmospheric reservoir and re-condenses, the likely outcome is precipitation that is depleted in heavy isotopes; an observation that is consistent with the isotope content of the 3 rainfall events sampled from the study area. Variation in the GMWL is often described by the d-excess, and therefore, values that are approximately less than 10 ‰ describe waters that have been evaporatively enriched whereas d-excess values for moisture contributed to the atmosphere are approximately greater than 10 ‰ (Deshpande et al., 2003; Marfia et al., 2004; Gupta et al., 2005; Dogramaci et al., 2012).

The LMWL of Akiti (1987) has been adopted as the LMWL in the study area, based on the fact that the study area has climatic and geographic conditions that are similar to those in the area where the LMWL was established. The intersection of the LMWL (Equation. 3.7) and the LEL (Equation. 3.8) produced an initial isotope content (Clark and Fritz, 1997; Jorgensen and Banoeng-Yakubo, 2001; Marfia et al., 2004; Dogramaci et al., 2012) of -29.68‰ δ^2H and -5.51‰ $\delta^{18}O$ that is more negative than the mean isotope composition of rainwater but comparable to the isotopic composition ($\delta^2H = -30.68\text{‰}$ and $\delta^{18}O = -4.88\text{‰}$) of the heaviest rainfall event collected

in May (RW05). Though the data collected on rainfall and lake water for this study is limited; the result suggests heavy rainfall events as the main source of water to the lake prior to evaporation. This agrees with the findings of Turner et al. (1996a) that the lake water input budget is dominated by heavy and intense rainfall events who estimated that about 80% of water that enters the lake annually is sourced from rainfall on its surface. The approximate rate of evaporation from the surface of the lake since its formation was estimated using the model proposed by Craig and Gordon (1965). This model, which has been used by many researchers in recent times (Dogramaci et al., 2012; Yidana, 2013), incorporates the local evaporation slope, initial isotopic signature of precipitation and the annual mean temperature for the area in calculating the evaporation loss. In the present study, the fraction lost to evaporation (f) was calculated from equation 3.9;

$$f = 1 - ((\delta_L - \delta^*) / (\delta_p - \delta^*))^{1/m} \dots\dots\dots 3.9$$

where δ^* is the local limiting isotopic signature (equation 3.10) calculated using the average relative humidity (h) of the area, the total isotope fractionation factor (ϵ) and the ambient air vapour isotope signature (δA) (Gat and Gonfiantini, 1981).

$$\delta^* = (h\delta A + \epsilon) / (h - \epsilon / 1000) \dots\dots\dots 3.10$$

δ_L and δ_p are the respective isotope signatures of sampled lake water and the source / initial water for the lake and the index, m , is given by equation 3.11

$$m = (h - \epsilon / 1000) / (1 - h + \epsilon_k / 1000) \dots\dots\dots 3.11$$

where ε_k is the kinetic isotope fractionation factor, which is related to the relative humidity between water (w) and water vapour (v) with respect to $\delta^{18}\text{O}$ is given by equation 3.12 (Gonfiantini, 1986)

$$\varepsilon_k^{18}\text{O}_{w-v} = 14.2(1-h) \text{‰} \dots\dots\dots 3.12$$

For the lake water in the study area, the $\varepsilon_k^{18}\text{O}_{w-v}$ returned a value of 4.97‰ at a local humidity of 0.7 (Turner et al., 1996a).

Also, ε sums both equilibrium and non equilibrium (kinetic) fractionation factors (equation 3.13).

$$\varepsilon = \varepsilon_{eq} + \varepsilon_k \dots\dots\dots 3.13$$

Where $\varepsilon_{eq} = 10^3(1 - \alpha^{18}\text{O}^{-1}_{w-v})$ and the fractionation factor $\alpha^{18}\text{O}_{w-v}$ between water and vapour is dependent on temperature (K) and expressed by equation 3.14 (Faure, 1998);

$$10^3 \ln \alpha^{18}\text{O}_{w-v} = (1.534 * 10^6) / T^2 + (3.206 * 10^3) / T + 2.644 \dots\dots\dots 3.14$$

At an average annual temperature of 25°C (298.15K), $\varepsilon_{eq} = 9.3\text{‰}$. The overall enrichment under the prevailing conditions was $\varepsilon = \varepsilon_{eq} + \varepsilon_k = -14.27\text{‰}$. A relationship between the initial precipitation, δ_{IP} and δA , proposed by Peng et al. (2012) presumes an isotopic equilibrium between δ_{IP} and δA as shown in Equation 3.15;

$$\delta A \cong \delta_{IP} - 10^3(\alpha_{w-v} - 1) \dots\dots\dots 3.15$$

Results obtained for RW04 sampled in April at Abono was taken as the isotopic signature of the first rainfall in the area and the δA value determined for $\delta^{18}\text{O}$ yielded -12.58‰. An estimated evaporation rate of ~82% from the surface of the lake is consistent with the high temperature and the low relative humidity of the area. The enriched isotopic signatures and increased concentration of the univalent cations in the lake water could be attributed to the evaporation rate, coupled with the possible hydrologically closed nature of the lake.

A regression line for groundwater in the study area is represented by Equation 3.16;

$$\delta^2H = 5.49\delta^{18}O + 4.33 \dots\dots\dots 3.16$$

Both the slope and intercept values of Equation 3.16 are lower than those of the MWLs, suggesting that rainwater available for recharge might have undergone evaporative enrichment either below the cloud base or within the unsaturated zone reaching isotopic signatures of the lighter rainfall (RW04) before it recharges the aquifers systems.

From an initial $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotope contents of -17.03‰ and -3.89‰ respectively, determined for the rainwater/precipitation that recharged the aquifers, evaporation rates ranging from 45-51% were estimated for the groundwater. This suggests that in the study area, almost half of the rainwater that begins transit through the unsaturated zone is lost to evaporation and aquifer recharge probably resulted from vertical infiltration or passage along flow paths in fractures. Thus rainwater available for groundwater recharge is reduced at most locations within the area. The calculated initial $\delta^{18}\text{O}$ (-3.89‰) is comparable to the mean value ($\delta^{18}\text{O} = -4.16‰$) of the

rainwater sampled from the study area, the mean $\delta^{18}\text{O}$ isotope content of -3.20‰ obtained by Akiti (1987) and the mean $\delta^{18}\text{O}$ value of -3.10 for groundwater from the study area. Statistically, these values are consistent with the characteristics of recent meteoric water. Thus, the groundwater might have been recharged by evaporated recent meteoric water through fissures and fractures in the rocks.

Figure 3.10 shows a general increase in EC without change in isotopic composition, indicating rock mineralization as controlling the chemistry of the groundwater and not evaporation hence the observed isotopic signature could result only from direct precipitation (Gibrilla et al., 2010).

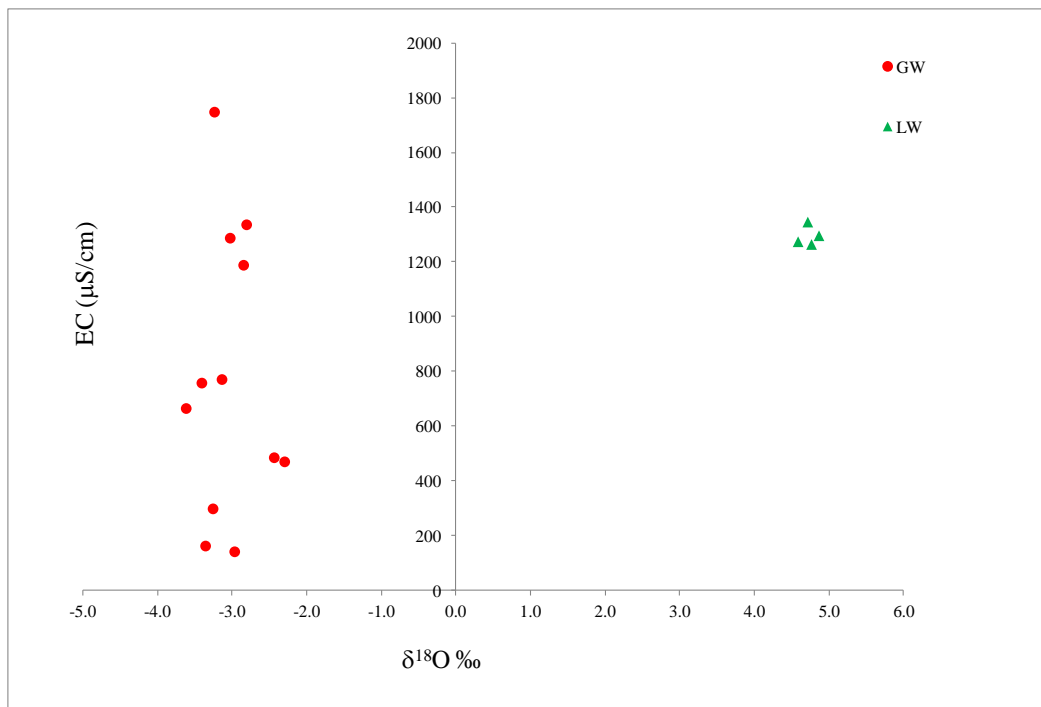


Fig. 3.10: Relationship between EC and $\delta^{18}\text{O}$ for the groundwater and lake water

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of groundwater in shallow boreholes located at lower elevations and in close proximity to the lake are significantly lighter than the lake water, but similar to those located on top of the crater rim (maximum elevation difference of ~ 300 m). Depletion gradients in the range of -1 to -4 ‰ for $\delta^2\text{H}$ and -0.15 to -0.6 ‰ for $\delta^{18}\text{O}$ per 100 m rise in elevation have been noted (Clark and Fritz, 1997; Dogramaci et al., 2012). However, Fig. 3.12 shows no such correlation suggesting that altitude has no effect on the isotope content of the groundwater. Based on this observation, it can be concluded that seepage from the evaporatively enriched lake water to the groundwater in aquifers in close proximity to the shore of the lake is possibly non-existent. This, however, does not rule out the possible hydraulic connection between the shallow aquifer system and the lake since groundwater may be contributing to the lake water.

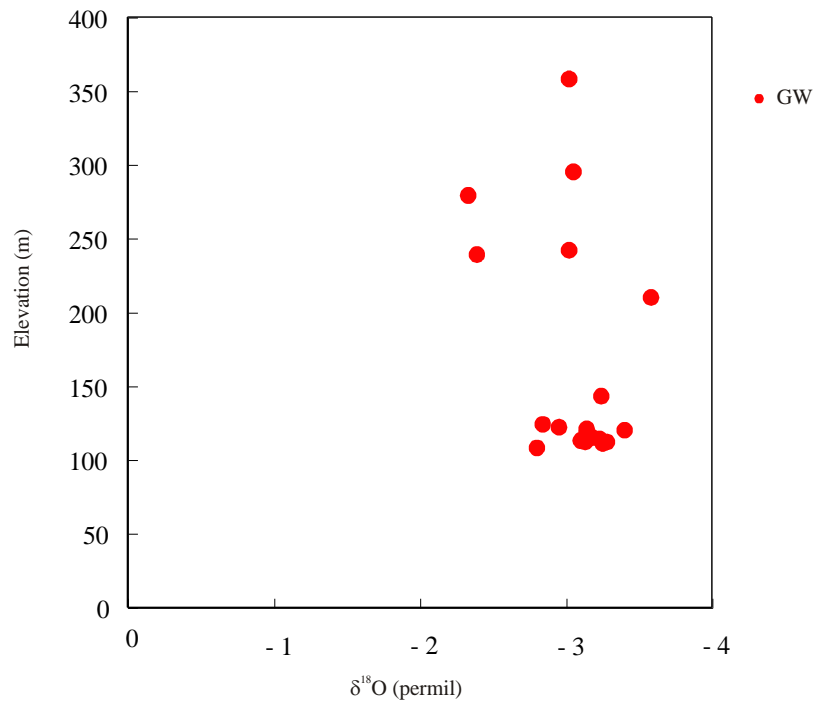


Fig. 3.12: Relationship between Elevation and $\delta^{18}\text{O}$ for the groundwater

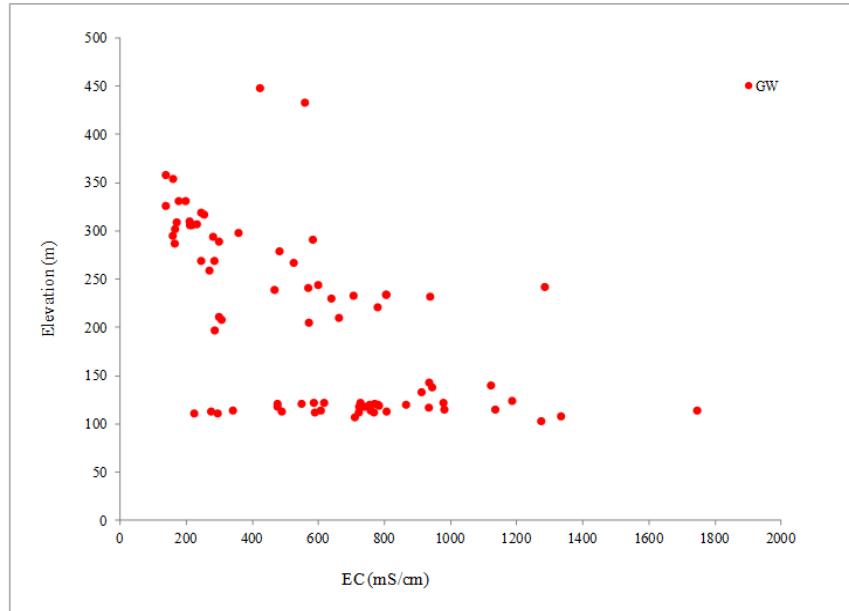


Fig. 3.13: Relationship between Elevation and EC for the groundwater

Figure 3.13 shows that the ionic contents of the groundwater generally increase towards lower elevations, indicating the direction of groundwater flow to the lake. This evolution identifies the top of the crater rim as a possible recharge area, thus corroborating the results from the cluster analysis (Fig. 3.3). If the groundwater really discharges into the lake then there is a possible hydraulic connection between these water bodies, and therefore proper aquifer/water management is required to forestall the possible seepage of lake water into the groundwater systems around the lake that may result from lowered hydraulic heads. This is possible because in the face of climate variability, changing land use pattern and urbanization, less water will be available to replenish the aquifers. Also, increase in population and human activities within the immediate vicinity of the lake will increase water demand and a subsequent increase in groundwater withdrawal. The reduction in recharge waters coupled with increased water

withdrawal may lower the groundwater head in the aquifer and the direction of groundwater flow will be reversed.

Conclusions

Hydrochemical and isotopic studies of groundwater and lake water from Bosumtwi impact crater has been carried out. Q-mode HCA performed on the samples revealed four main clusters based on the spatial variations in their hydrochemistry. The results indicate that recharge to the aquifers is by direct infiltration of evaporated recent meteoric water through fractures in the unsaturated zone to the saturated zone. Recharge occurs on the hill tops and the groundwater evolves chemically to lower elevations within the morphological crater rim and its mineralization is controlled by minerals of the host rocks. Evaporation rates of 45-51% estimated for the groundwater do not influence the chemistry of the groundwater of the area. The lake water on the other hand, is evaporatively enriched, and thus clusters exclusively from the groundwater with respect to both chemical and isotopic composition and cannot explain the hydrochemistry of groundwater in the area particularly those in close proximity to the lake. The isotope data of the lake indicates considerable enrichment in relation to local meteoric water, and suggests evaporation rate of 82% from the open lake surface resulting in increased concentration of the univalent cations. The study also established that any hydraulic connection between the two reservoirs may not benefit the aquifers in the area, although the converse is likely. This finding is at variance with an earlier assumption that suggested lake water seepage to the boreholes in the immediate vicinity of the lake.

References

- Abid, K., Zouari, K. and Abidi, B. 2010. Identification and characterisation of hydrogeological relays of continental intercalaire aquifer of southern Tunisia. *Carbonates and Evaporites*, 25(1), 65-75.
- Akiti, T. T., 1987. Environmental isotope study of groundwater in crystalline rocks of the Accra Plains (Ghana) *In: Wand U and G, S. eds. Isotopes in nature*. Leipzig: Academy of Sciences of the GDR, Central Institute of Isotope and Radiation Research, 107-121.
- Appelo, C. A. J. and Postma, D., 2005. *Geochemistry, groundwater and pollution*. . 2nd ed. Balkema, Rotterdam.
- Berry, J. K., 1995. Spatial reasoning for effective GIS. . . *GIS World Book*. Colorado Fort Collins.
- Boamah, D. and Koeberl, C., 2002. Geochemistry of Soils from the Bosumtwi Impact Structure, Ghana, and Relationship to Radiometric Airborne Geophysical Data. *In: Plado, J. and Pesonen, L. eds. Impacts in Precambrian Shields*. Springer Berlin Heidelberg, 211-255.
- Butler, M. J., Verhagen, B. T. and Levin, M., Application of environmental isotopes to hydrological and pollution problems in the urban environment. . ed. *Groundwater: Past Achievements and Future Challenges*, 2000 Balkema, Rotterdam, 459-464.
- Cartwright, I., Hall, S., Tweed, S. and Leblanc, M. 2009. Geochemical and isotopic constraints on the interaction between saline lakes and groundwater in southeast Australia. *Hydrogeology Journal*, 17(8), 1991-2004.

- Chen, Z., Nie, Z., Zhang, G., Wan, L. and Shen, J. 2006. Environmental Isotopic Study on the Recharge and Residence time of Groundwater in the Heihe River Basin, northwestern China *Hydrogeology Journal*, 14(8), 1635-1651.
- Clark, I. D. and Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. New York: Lewis Publishers.
- Coplen, T. B. 1994. Reporting of Stable Hydrogen, Carbon, and Oxygen Isotopic Abundances. *Pure and Applied Chemistry*, 66, 273-276.
- Coplen, T. B. and 1993. Uses of environmental isotopes. *In: W.M.Alley ed. Regional groundwater quality*. New York: Van Nostrand Reinhold 227-254.
- Corp, I., 2011. IBM SPSS Statistics for Windows. 20 ed. Armonk, NY IBM Corp.
- Craig, H. 1961. Isotope variations in Meteoric waters. *Science*, 133, 1702-1703.
- Craig, H. and Gordon, L. I., Deuterium and oxygen 18 variations in the ocean and marine atmosphere. ed. *Stable Isotopes in Oceanographic Studies and Paleotemperatures*, 1965 Spoleto, Italy, 9-130.
- Dansgaard, W. 1964. Stable isotope in precipitation. . *Tellus*, 16, 436-469.
- Demlie, M., Ayenew, T. and Wohnlich, S. 2007. Comprehensive hydrological and hydrogeological study of topographically closed lakes in highland Ethiopia: The case of Hayq and Ardibo. *Journal of Hydrology*, 339(3-4), 145-158.

- Demlie, M., Wohnlich, S. and Ayenew, T. 2008. Major ion hydrochemistry and environmental isotope signatures as a tool in assessing groundwater occurrence and its dynamics in a fractured volcanic aquifer system located within a heavily urbanized catchment, central Ethiopia. *Journal of Hydrology*, 353(1-2), 175-188.
- Deshpande, R. D., Bhattacharya, S. K., Jani, R. A. and Gupta, S. K. 2003. Distribution of oxygen and hydrogen isotopes in shallow groundwaters from Southern India: influence of a dual monsoon system. *Journal of Hydrology*, 271 226-239.
- Dincer, T., Noory, M., Jaret, A. R. K.' Nuti, S. and Tongiorgi, E.1978. Study, using stable isotopes of flow distribution, surface-groundwater relations and evapotranspiration in the Okavango Swamp, Botswana.ed. *Isotope Hydrology Proc. Intern. Symp. Neuherberg*, 19-23 June 1978 1978 International Atomic Energy Agency, Vienna.
- Dogramaci, S.Skrzypek, G., Dodson, W. and Grierson, P. F. 2012. Stable isotope and hydrochemical evolution of groundwater in the semi-arid Hamersley Basin of subtropical northwest Australia. *Journal of Hydrology*, 475, 281-293.
- Edmunds, W. M., Bath, A. H. and Miles, D. K. 1982. Hydrochemical evolution of the East Midlands Triassic sandstone aquifer, England. . *Geochem Cosmochim Acta*, 46, 2069-2082.
- Faure, G., 1998. *Principles and Applications of Geochemistry*. 2nd ed. New Jersey: Prentice-Hall.
- Field, A., 2005. *Discovering Statistics Using SPSS*. Second ed. London, Thousand Oaks, New Delhi: SAGE Publications.

- Fontes, J. C., Environmental isotopes in groundwater hydrology. ed. *Environmental Isotope Geochemistry*, 1980, 75-140.
- Freeze, A. R. and Cherry, J. A., 1979. *Groundwater*. New Jersey: Prentice-Hall.
- Garrels, R. M. and Mackenzie, F. T. 1967. Origin of the chemical composition of some springs and lakes. In: Equilibrium concepts in natural-water chemistry. Advances in Chemistry Series, . *American Chemical Society*, (67), 222-242.
- Gat, J. R. and Gonfiantini, R., 1981. *Stable isotope hydrology: deuterium and oxygen-18 in the water cycle*. . Vienna: IAEA, 210.
- Gibrilla, A., *et al.* 2010. Origin of Dissolve Ions in Groundwaters in the Northern Densu River Basin of Ghana Using Stable Isotopes of ^{18}O and ^2H . *J. Water Resource and Protection*, 2, 1010-1019.
- Gonfiantini, R., ed., 1986. *Environmental isotopes in lake studies*. New York: Elsevier.
- Gosselin, D. C., Harvey, F. E. and Frost, C. D. 2001. Geochemical evolution of groundwater in the Great Plain aquifer of Nebraska: implications for the management of the regional aquifer system. . *Ground Water*, 39(1), 98-108.
- Guay, B. E., Eastoe, C.J., Bassett, R. and Long, A. 2006. Identifying sources of groundwater in the lower Colorado River valley, USA, with $\delta^{18}\text{O}$, δD and ^3H : implications for river water accounting. *Hydrogeology Journal*, 14, 146-158.

- Guler, C., Thyne, G. D., McCray, J. E. and Turner, A. K. 2002. Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. *Hydrogeology Journal*, 10(4), 455-474.
- Gupta, S. K., Deshpande, R. D., Bhattacharya, S. K. and Jani, R. A. 2005. Groundwater $\delta^{18}\text{O}$ and δD from central Indian Peninsula: influence of the Arabian Sea and the Bay of Bengal branches of the summer monsoon. *Journal of Hydrology*, 303(1-4), 38-55.
- Helstrup, T., Jørgensen, N. O. and Banoeng-Yakubo, B. 2007. Investigation of hydrochemical characteristics of groundwater from the Cretaceous-Eocene limestone aquifer in southern Ghana and southern Togo using hierarchical cluster analysis. *Hydrogeology Journal*, 15(5), 977-989.
- Hem, J. D., 1989. *Study and interpretation of chemical characteristics of natural waters*.
- Hendry, M. J. and Schwartz, F. W. 1990. The chemical evolution of groundwater in the Milk River Aquifer, Canada. . *Ground Water*, 28(2), 253-261.
- Herczeg, A. L., Simpson, H. J. and Mazor, E. 1993. Transport of soluble salts in large semiarid basin; River Murray, Australia. . *Journal of Hydrology*, 144 59-84.
- Hirdes, W., Davis, D. W. and Eisenlohr, B. N. 1992. Reassessment of Proterozoic granitoid ages in Ghana on the bases of U/Pb zircon and monazite dating. *Precambrian Research*, 56, 89-96.
- Hiscock, K. M., Dennis, P. F., Saynor, P. R. and Thomas, M. O. 1996. Hydrochemical and stable isotope evidence for the extent and nature of the effective chalk aquifer of north Norfolk, UK. *Journal of Hydrology*, 180, 79-107.

- Hoefs, J., 2009 *Stable Isotope Geochemistry*. 6 ed.: Springer-Verlag Berlin Heidelberg.
- IAEA, 1983. *Guidebook on Nuclear Techniques in hydrology*. Vienna: IAEA, 91.
- Jones, W. B., Bacon, M. and Hastings, D. A. 1981. The Lake Bosumtwi impact crater, Ghana. *Geological Society of America Bulletin*, 92(6), 342.
- Jorgensen, N. O. and Banoeng-Yakubo, B. K. 2001. Environmental isotopes (^{18}O , ^2H , and $^{87}\text{Sr}/^{86}\text{Sr}$) as a tool in groundwater investigations in the Keta Basin, Ghana. *Hydrogeology Journal*, 9, 190-201.
- Judd, A. D. 1980. The use of cluster analysis in the derivation of geotechnical classifications. *Bull Assoc Eng Geol*, 17, 193-211.
- Karikari, F., Ferrière, L., Koeberl, C., Reimold, W. U., and Mader, D. 2007. Petrography, geochemistry, and alteration of country rocks from the Bosumtwi impact structure, Ghana. *Meteoritics & Planetary Science*, 42(4-5), 513-540.
- Kesse, G. O., 1985. *The mineral and rock resources of Ghana*. Boston: Rotterdam, A.A. Balkema.
- Koeberl, C., Reimold, W. U., Blum, J. D. and Chamberlain, P. C. 1998. Petrology and geochemistry of target rocks from the Bosumtwi impact structure, Ghana, and comparison with Ivory Coast tektites. *Geochimica et Cosmochimica Acta*, 62(12), 2179-2196.

- Leube, A., Hirdes, W. Mauer, R. and Kesse, G. O.1990. The early Proterozoic Birimian Supergroup of Ghana and some aspects of its associated gold mineralization. *Precambrian Research*, 46, 139-165
- Loh, Y. S., Banoeng-Yakubo, B., Yidana, S. M. , Asiedu, D., Akabzaa, T. and Jørgensen, N. O.2012. Hydrochemical Characterisation of Groundwater in Parts of the Volta Basin, Northern Ghana. *Ghana Mining Journal*, 13, 24 - 32.
- Marfia, A. M., Krishnamurthy, R. V., Atekwana, E. A. and Panton, W. F. 2004. Isotopic and geochemical evolution of ground and surface waters in a karst dominated geological setting: a case study from Belize, Central America. *Applied Geochemistry*, 19(6), 937-946.
- Mazor, E., 1997. *Chemical and isotopic groundwater hydrology*. 3rd ed. New York: Marcel Dekker, Inc.
- Ojiambo, S. B., Poreda, R. J. and Lyons, W. B. 2001. Ground Water/Surface Water interactions in Lake Naivasha, Kenya, Using d¹⁸O and dD. *Ground Water*, 39(4), 526-533.
- Panno, S. V.,Hackley, K. C., Cartwright, K. and Liu, C. L.1994. Hydrochemistry of the Mahomet bedrock valley aquifer, East-Central Illinois: Indicators of recharge and groundwater flow. *Ground Water*, 32(4), 591-604.
- Peng, T. R.,Huang, C. C., Wang, C. H., Liu, T. K. and Lu, W. C. 2012. Using oxygen, hydrogen, and tritium isotopes to assess pond water's contribution to groundwater and local precipitation in the pediment tableland areas of northwestern Taiwan. . *Journal of Hydrology*, 450-451, 105-116.

- Petrides, B., Cartwright, I. and Weaver, T. R. 2006. The evolution of groundwater in the Tyrrell catchment, south-central Murray Basin, Victoria, Australia. *Hydrogeology Journal*, 14(8), 1522-1543.
- Reimold, W. U., Brandt, D. and Koeberl, C. 1998. Detailed structural analysis of the rim of a large, complex impact crater: Bosumtwi Crater, Ghana. *Geology*, 26, 543-546.
- Rummel, R. J., 1970. *Applied factor analysis*. . Evanston: Northwestern University Press.
- Sophocleous, M. 2002. Interactions between groundwater and surface water: the state of the science. *Hydrogeology Journal*, 10(1), 52-67.
- Stichler, W. and Moser, H., 1979. An example of exchange between lake and groundwater, Isotopes in lake studies. *Proc. Panel Vienna*,. IAEA, Vienna.
- Stimson, J., Frapce, S., Drimmie, R. and Rudolph, D.2001. Isotopic and geochemical evidence of regional-scale anisotropy and interconnectivity of an alluvial fan system, Cochabamba Valley, Bolivia. *Applied Geochemistry*, 16, 1097-1114.
- Stuyfzand, P. J. 1999. Patterns in Groundwater chemistry resulting from groundwater flow. *Hydrogeology Journal*, 7, 15-27.
- Sukhija, B. S.,Reddy, D. V. Nagabhushanam, P. Bhattacharya, S. K. Jani, R. A. and Kumar, D.2005. Characterisation of recharge processes and groundwater flow mechanisms in weathered-fractured granites of Hyderabad (India) using isotopes. *Hydrogeology Journal*, 14(5), 663-674.

- Turner, B., Gardner, L., Sharp, W. and Blood, E. 1996a. The geochemistry of Lake Bosumtwi, a hydrologically closed basin in the humid zone of tropical Ghana. *Limnology and Oceanography*, 41(7), 1415-1424.
- Turner, B. F., Gardner, L. R. and Sharp, W. E. 1996b. The hydrology of Lake Bosumtwi, a climate-sensitive lake in Ghana, West Africa. *Journal of Hydrology*, 183(3-4), 243-261.
- Wagner, R., Reimold, W. and Brandt, D., 2002. Bosumtwi Impact Crater, Ghana: A Remote Sensing Investigation. In: Plado, J. and Pesonen, L. eds. *Impacts in Precambrian Shields*. Springer Berlin Heidelberg, 189-210.
- Yidana, S. M. 2013. The Stable Isotope Characteristics of Groundwater in the Voltaian Basin – An Evaluation of the Role of Meteoric Recharge in the Basin. *Journal of Hydrogeology & Hydrologic Engineering*, 2(2), 1-10.
- Yidana, S. M., Banoeng-Yakubo, B. and Asamoah Sakyi, P. 2012a. Identifying key processes in the hydrochemistry of a basin through the combined use of factor and regression models. *Journal of Earth System Science*, 121(2), 491-507.
- Yidana, S. M., Ophori, D. and Banoeng-Yakubo, B. 2008. A Multivariate Statistical Analysis of Surface Water Chemistry Data—The Ankobra Basin, Ghana *J Environ Manage*, 86(1), 80- 87.
- Yidana, S. M., Ophori, D., Banoeng-Yakubo, B. and Samed, A. A.. 2012b. A Factor Model to Explain the Hydrochemistry and Causes of Fluoride Enrichment in Groundwater from the

Middle Voltaian Sedimentary Aquifers in the Northern Region, Ghana. *ARPJ Journal of Engineering and Applied Sciences*, 7(1), 50-68.

CHAPTER FOUR

DETERMINATION OF THE MINERAL STABILITY FIELD OF EVOLVING GROUNDWATER IN THE LAKE BOSUMTWI IMPACT CRATER AND SURROUNDING AREAS

Abstract

Conventional graphical techniques, mass balance geochemical modelling, and multivariate statistical methods were jointly applied to hydrogeochemical data of groundwater from the fractured rock aquifer system, and surface water in the Bosumtwi and surrounding areas to reveal evolutionary trends and the characteristics of evolving groundwater in the area. Four clusters distinguished from Q-mode hierarchical cluster analysis (HCA) comprised three main groundwater associations and one surface water group (lake water). Although both water resources are of low mineralisation (TDS < 1000 mg/l), it was observed that the groundwater from the upper catchment with hydrochemical facies dominated by Na-Mg-HCO₃⁻, evolves to Ca-Mg- and mixed cations HCO₃⁻ water types at the lower reaches. The lake water on the other hand is Na-HCO₃⁻ water type. Results from principal component analyses (PCA) and other geochemical interpretations distinguished three sources of variations in the hydrochemistry. Saturation indices of possible reactive mineral phases show groundwater undersaturation relative to albite, anorthite, aragonite, barite, calcite, chlorite, chrysotile, dolomite, gypsum, k-feldspar and talc, and supersaturation with respect to gibbsite, kaolinite, Ca-montmorillonite and k-mica in the area. The PCA and other geochemical interpretation identify incongruent weathering of feldspars and carbonate mineral dissolution as predominantly influencing the hydrochemistry of the

groundwater. Hydrolysis of the aluminosilicates causes the groundwater to reach equilibrium with kaolinite. In addition to incongruent dissolution of silicates, the chemical composition of the lake water have been influenced by evaporation and consequent carbonate saturation

4.1 Introduction

The chemical composition of natural waters is controlled by a variety of factors that include the composition of rainwater, climate, topography, structure and mineralogy of host rocks and the geochemical processes that are operating within the aquifers. These factors can combine in various ways to give the water a characteristic fingerprint, consequently determining the purpose for which it can be used. Interpretation of hydrochemical data from regional aquifer sampling and analyses has provided useful leads to understanding groundwater evolution along flow paths (Gerla, 1992; Marfia et al., 2004; Salem et al., 2004). The literature is rich in several innovative methods to aid the interpretation of the hydrochemical data. In addition to conventional graphical methods, the application of multivariate statistical techniques to physical and chemical data of natural waters to uncover latent characteristics that assist in groundwater and surface water evolution has been copiously documented in the literature (e.g. Thyne et al., 2004; Cloutier et al., 2008; Yidana et al., 2011). The advanced statistical approaches commonly used in the geosciences are discretionary and are able to cluster hydrochemical parameters into groups, associations or hierarchies based on the variations in the datasets of those parameters. When used simultaneously with conventional graphical techniques, advanced statistical methods assist in identifying key hydrogeological processes that play in the transformation of the hydrochemistry of groundwater along flow paths (e.g. Guler et al., 2002; Thyne et al., 2004; Yidana et al., 2012). Stetzenbach et al. (1999) applied the multivariate statistical method; principal component

analyses (PCA), to hydrochemical dataset and concluded that PCA is not only used to support previously studied hydrological systems but may in itself provide rapid and relatively cost effective methods to assess possible flow regimes in systems that have not been previously studied. Suk and Lee (1999) discretised and characterised the groundwater hydrochemical system of an area in Incheon, Korea, through cluster analysis using factor scores.

Over the last decade, mass balance hydrochemical modelling, particularly using PHREEQC, has proven a powerful tool for chemical simulation (Van der Kemp et al., 2000; Wurl et al., 2003; Dai and Samper, 2004; Lecomte et al., 2005). The method has been valuable in computing aqueous speciation and saturation indices from geochemical data to determine the reactive minerals within aquifers (Thyne et al., 2004; Yidana et al., 2008b; Ako et al., 2011). Saturation indices have been useful in evaluating the degree of equilibrium between water and aquifer minerals, distinguish different stages of hydrochemical evolution (Locsey and Cox, 2002) and assist in identifying which geochemical reactions are important in surface and groundwater hydrochemistry (Yidana et al., 2008a; Aghazadeh and Mogaddam, 2010). Whiles Busby et al., (1991) used the mass balance technique to quantify reactions controlling water chemistry along flow paths; Kuells et al., (2000) applied the technique to quantify mixing of end-member components in a flow system. Thyne et al. (2004) employed integrated statistical and mass balance methods to identify natural water/rock interaction and an anthropogenic component as the major processes controlling the hydrochemistry in aquifers along the Turkey Creek Basin, to determine the location and chemical signature of anthropogenic impact, and provide information about the aquifer properties. Similarly, Helstrup et al. (2007) identified the most relevant controls on the water quality within the Cretaceous-Eocene limestone aquifer of the Keta Basin of Ghana

and the coastal sedimentary basin of Togo, using Q-mode hierarchical cluster analysis (HCA) and mass-balance modelling methods.

In most parts of Ghana, particularly aquifers underlying the Bosumtwi Impact Crater (BIC) and surrounding areas, there is general lack of hydrologic and hydrogeologic data which has resulted in great uncertainties in the understanding of the groundwater flow regimes and also in the understanding of the main processes that influence the hydrochemical evolution of groundwater. In fact since the construction of boreholes and use of groundwater in the study area, no investigations have been conducted over the years to accurately characterise the groundwater resources with respect to the hydrochemistry. Such a study will not only better define the mode of groundwater occurrence but will assist in understanding the behaviour of groundwater from recharge to discharge areas as this is key to developing an effective water use system and in the planning and management of groundwater resources of the area. Conventional methods, coupled with multivariate statistical, PHREEQC modelling and stability diagrams have been applied to hydrogeochemical data collected for this study to characterize the groundwater systems and evaluate the principal controls on groundwater and lake water hydrochemistry to present an enhanced understanding of the hydrology of the study area's watershed. It is envisaged that results from this research will assist policy / decision makers to develop a better management plan that will ensure sustainable use of the groundwater resources in the study area.

4.2 Materials and Methods

The sampling program was designed to obtain information about the spatial variability of dissolved phases. In all, 34 groundwater and 7 lake water samples were collected between July

15 and August 5, 2012 for this study. Sampling and analytical procedures have been described in Chapter 2 (Section 2.2).

Hydrogeochemical data is multivariate in character thus multivariate statistical analyses of the data examined the relationships among variables and brought out the intrinsic interdependence between observations (either cases or variables) with emphasis on revealing natural groupings/clusters within the data set that would otherwise not be noticeable. Hierarchical Cluster Analysis (HCA), discussed in Section 3.2 and Principal Component Analysis (PCA) were made using the statistical software package SPSS 20 for Windows (Corp, 2011). PCA was performed on the dataset to trim down the number of variables to a small number of new, uncorrelated variables. These new set of variables that occur from the linear combination of the original variables are the Principal Components (PCs). In this way, relationships among the variables and/or samples are established and the contribution of each one or of each combination in the structure of the hydrochemical data is defined. Using Kaiser criterion (Kaiser, 1960), the PCs were extracted and rotated using varimax normalisation. Only components with eigenvalues greater than or equal to 1 were accepted as possible sources of variance in the data. The reason for choosing 1 is that a component must have a variance at least as large as that of a single standardise original variable to be acceptable. The highest priority is then ascribed to the component with the highest eigenvector sum. The varimax rotation ensured that variation in the data was maximized for easy interpretation of the results (Yidana et al., 2008b).

The geochemical computer code PHREEQC version 2 (Parkhurst and Appelo, 1999) was then used to model the hydrochemistry based on the concentrations of both major and minor ions in solution. The mineral saturation indices (SI) are expressed as;

$$SI = \log \frac{IAP}{K_{sp}} \dots\dots\dots 4.1$$

where IAP is the ion activity product of ionic species in solution and K_{sp} is the solubility product of a mineral. The system is said to be undersaturated with SI less than 0. When SI is 0, the mineral is saturated and the K_{sp} just equals the IAP. With SI's higher than 0, the system is supersaturated with respect to the minerals in question.

4.3 Results and Discussions

The univariate overview of the physico-chemical parameter presented in a box plot shows the minimum, median, maximum, 25th and 75th percentiles of measured parameters (Fig. 4.1). Though low groundwater pH (< 6 pH units) were recorded at some locations, particularly samples from the upper catchment, all other parameters measured for the groundwater in this study have concentrations that fall within the guideline values recommended by WHO (2011) for drinking and other domestic purposes. The spatial variation in the hydrochemistry determined by Q-mode HCA resulted in four spatial associations (clusters 1 to 4) when a phenon line was

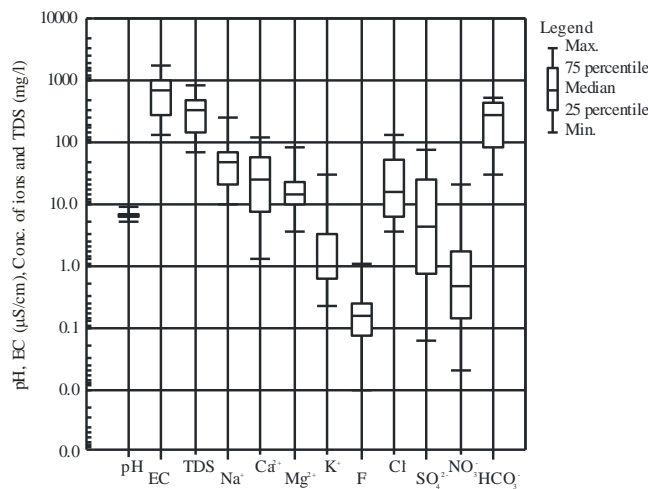


Fig. 4.1: Box plot for the physical and major ions for the water samples from the study area

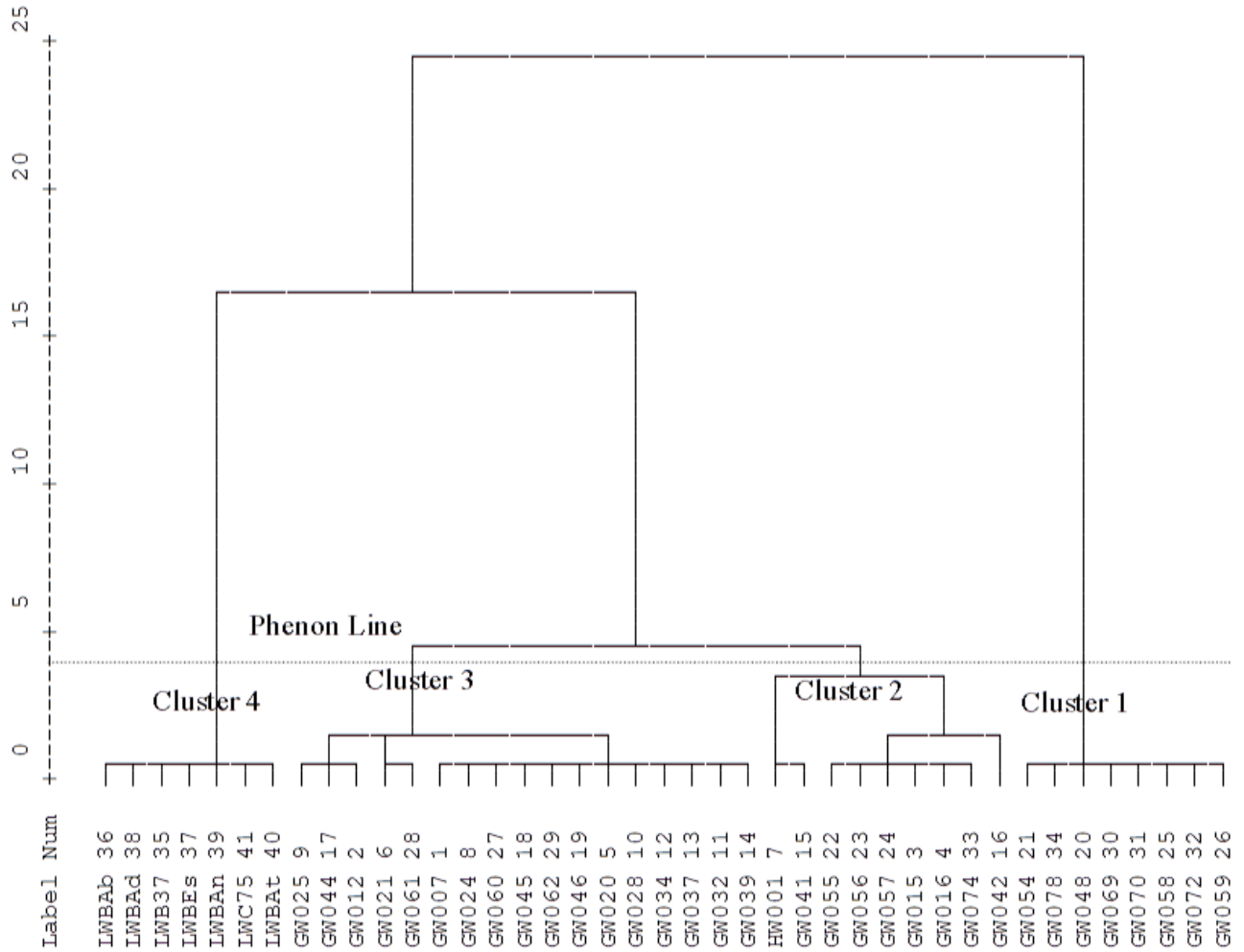


Fig. 4.2: Dendrogram generated from HCA of hydrochemical data from groundwater (Clusters 1 to 3) and lake water (Cluster 4) showing associations between the samples.

drawn at a linkage distance of 4.8 (Fig.4.2). These clusters explained most of the variations in the hydrochemical properties of the water samples. Samples in the same cluster are either located in close proximity to each other (Fig. 4.3) or at similar elevation indicating similar processes or flow paths. Stiff diagrams made from the arithmetic means of the measured parameters illustrate

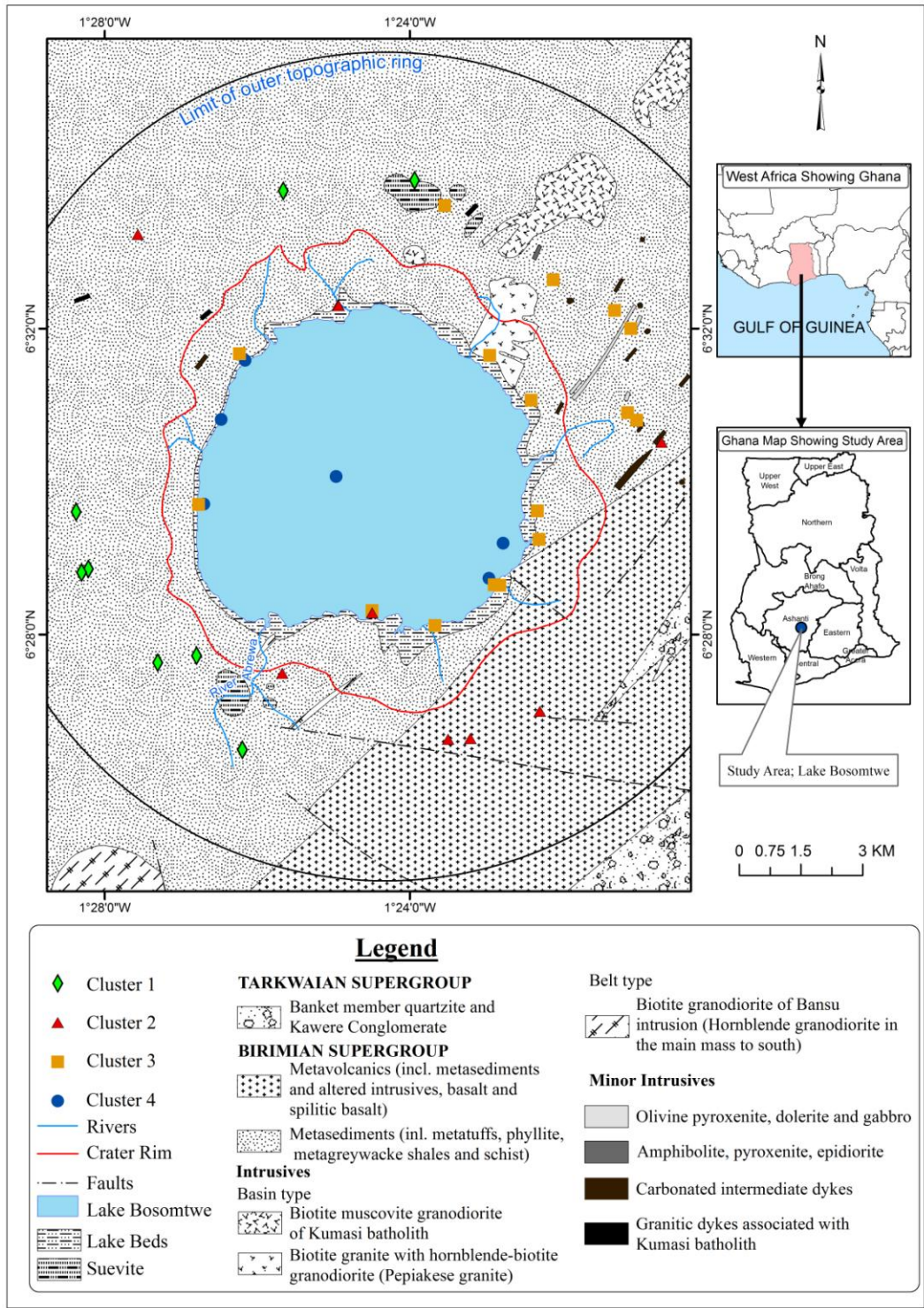


Fig. 4.3: Map showing the spatial distribution of samples based on clusters

the comparative distribution pattern of the dissolved major ions for each cluster (Fig. 4.4). The distribution of anions for all the clusters is in the order of $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ irrespective of the level of mineralization. The HCO_3^- ion concentration for all clusters is about ten to fifteen times the concentration of Cl^- . The enrichment of the groundwater by bicarbonate compared to chloride or sulphate may be attributed to groundwater derived from direct recharge of rainwater through the overburden to the underlying aquifers. The recharge process appears to be rapid and does not provide for long residence time in order for active water-rock interaction to occur. This is particularly true for samples of cluster 1.

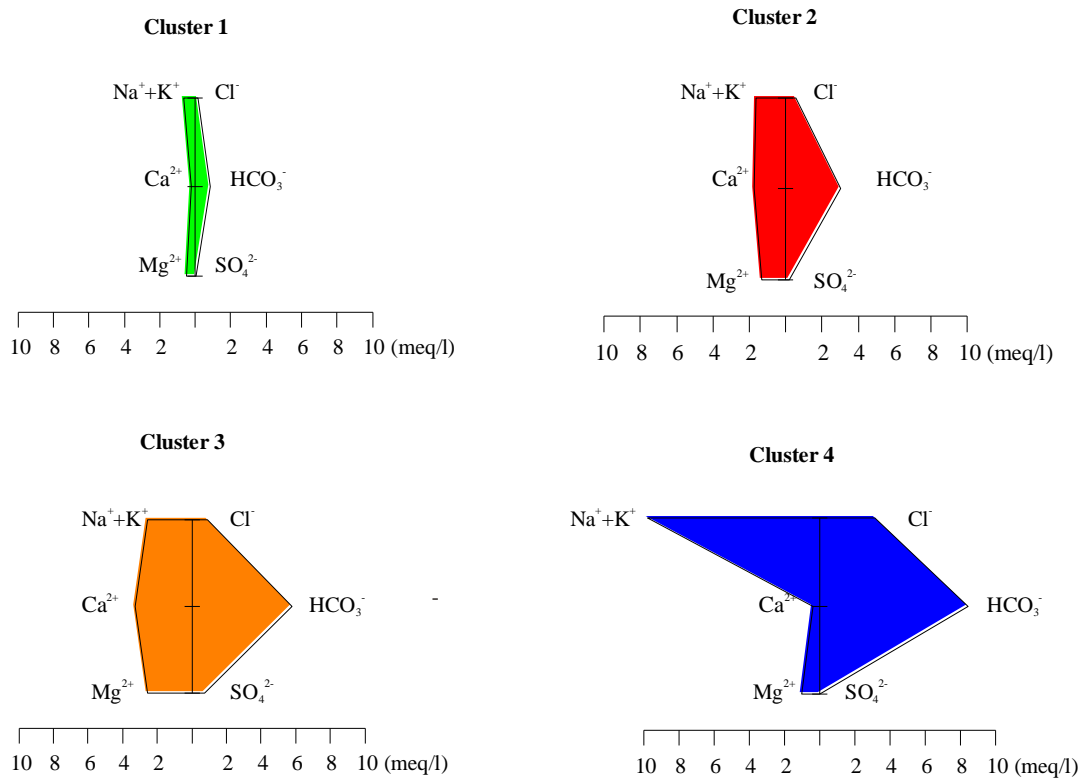


Fig. 4.4: Stiff diagrams from the mean of the major ions in the four clusters from the Q-mode HCA

The cations on the other hand exhibit slight variations. Cluster 1 (C1) and cluster 4 (C4) samples are similarly distributed in an order of $(\text{Na}^+ + \text{K}^+) > \text{Mg}^{2+} > \text{Ca}^{2+}$. Cluster 2 (C2) was found to be $\text{Ca}^{2+} \geq (\text{Na}^+ + \text{K}^+) > \text{Mg}^{2+}$ and cluster 3 (C3) as $\text{Ca}^{2+} > (\text{Na}^+ + \text{K}^+) \geq \text{Mg}^{2+}$ (Fig. 4.4). The samples were then classified into hydrochemical facies on the basis that the dominant major cations and anion exceed 50% of total cations and anions respectively (Fig. 4.5). The figure classifies the lake water (C4) as Na-HCO_3^- water type. Majority of C1 groundwater samples are in the Na-Mg-HCO_3^- portion of the diagram; hence are Na-Mg-HCO_3^- water types whiles C2 and C3 are of Ca-Mg- and mixed cations HCO_3^- water types.

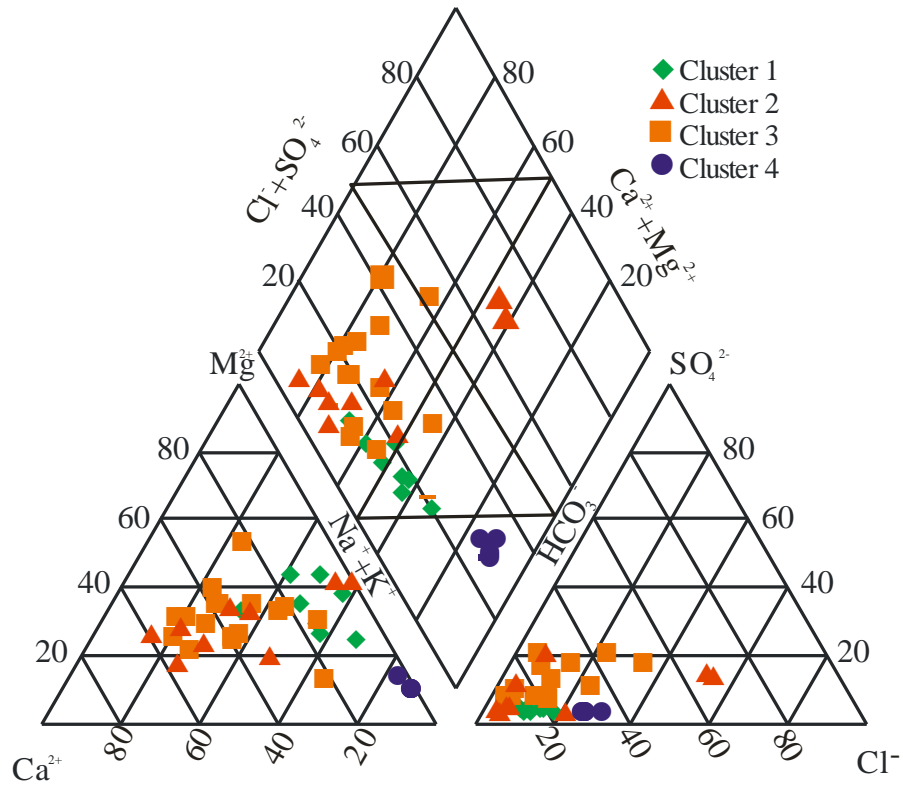


Fig. 4.5: Piper trilinear diagram showing the hydrochemical facies according to their clusters in the area

Table 4.1: Saturation indices of possible reactive mineral phases in the groundwater and lake water samples from the study area.

C1 Samples	Anor		Arago		Ca- montmo		Chalce		Chryso Dolo		Fe	Gibbs		K-		Kaoli		Side		Goeth Gyp		
	Albite	thite	nite	Barite	rillonite	Calcite	dony	Chlorite	tile	mite	(OH)3(a)	ite	illite	Feldspar	k-Mica	nite	Qtz	rite	Silica (a)	Talc	ite	sum
GW054	-5	-11	-5.89	-2.75	-0.67	-5.74	0.18	-30.57	-19.73	-10.6	-4.46	-0.14	-3.66	-4.1	1.22	1.75	0.58	-4.6	-0.66	-15.7	1.43	-5.7
GW078	-5.89	-12	-5.94	-3.55	-2.32	-5.8	0.15	-29.7	-18.45	-10.3	-5.49	-0.81	-5.37	-5.17	-1.18	0.36	0.55	-5.8	-0.69	-14.5	0.42	-5.9
GW048	-4.21	-9.2	-4.06	-1.85	-0.38	-3.92	0.28	-24.71	-16.04	-7.44	-2.23	-0.29	-2.94	-3.25	1.78	1.65	0.68	-2.7	-0.56	-11.8	3.66	-4.2
GW070	-3.4	-7.1	-3.57	-2.4	1.57	-3.43	0.31	-22.05	-15.34	-6.77	-1.74	0.45	-1.06	-2.42	4.1	3.21	0.71	-2.4	-0.53	-11	4.17	-4.6
GW069	-3.48	-8.3	-3.95	-2.58	0.61	-3.8	0.4	-23.17	-15.36	-7.26	-1.14	-0.08	-1.87	-2.48	2.98	2.33	0.8	-1.8	-0.44	-10.9	4.76	-4.6
GW072	-3.81	-8.6	-4.59	-2.51	0.68	-4.45	0.31	-25.53	-17.04	-8.6	-3.78	0.12	-2.03	-2.86	2.99	2.55	0.72	-4.5	-0.52	-12.7	2.14	-4.8
GW058	-2.35	-6.4	-4.54	-2.74	3.26	-4.39	0.4	-22.3	-16.1	-8.26	-3.42	1.1	0.39	-1.93	5.88	4.67	0.8	-4.2	-0.44	-11.6	2.51	-4.5
GW059	-3.04	-7.6	-3.96	-1.62	1.58	-3.82	0.48	-21.52	-14.72	-7.08	-3.87	0.22	-0.47	-1.29	4.76	3.08	0.88	-4.4	-0.36	-10.1	2.05	-4.2
C2 Samples																						
HW001	-2.88	-7.4	-4.35	-1.44	1.86	-4.2	0.24	-20.99	-15.06	-7.47	-3.31	0.73	-0.68	-2.43	4.64	3.63	0.65	-3.8	-0.59	-10.9	2.61	-3.4
GW041	-3.2	-8.2	-4.62	-1.12	1.09	-4.48	0.18	-20.75	-14.73	-7.52		0.53	-1.37	-2.87	3.08	3.09	0.58		-0.65	-10.6		-3.8
GW015	-1.55	-3.1	-1.37	-1.93	3.74	-1.23	0.14	-9.26	-9.02	-2.35	-0.7	1.5	1.92	-0.75	7.89	4.95	0.53	-2.1	-0.69	-5.01	5.29	-2.6
GW024	-1.84	-3.8	-1.37	-1.35	2.75	-1.23	0.04	-9.43	-8.84	-2.15		1.23	1.07	-1.27	6.82	4.22	0.43		-0.79	-5.02		-2.7
GW016	-2.21	-4.4	-2.35	-1.31	3.03	-2.2	0.15	-13.71	-11.38	-4.25	-1.43	1.23	0.95	-1.41	6.67	4.44	0.55	-2.7	-0.67	-7.33	4.58	-2.7
GW057	-2.93	-4.4	-0.72	-1.59	1.39	-0.58	-0.09	-9.57	-8.37	-1.3	0.76	0.81	-0.36	-2.2	5.04	3.12	0.31	-1	-0.93	-4.85	6.68	-3.1
GW055	-3.04	-6	-1.79	-2.14	1.29	-1.64	0.21	-17.68	-12.64	-3.71	-1.26	0.39	-1.21	-2.61	3.79	2.89	0.62	-2.1	-0.63	-8.49	4.61	-3.2
GW056	-1.98	-3.6	-0.67	-1.94	2.85	-0.53	0.22	-9.28	-8.28	-1.31	1.32	0.95	1.12	-0.93	6.58	4.03	0.63	-0.2	-0.62	-4.14	7.21	-3.4
GW074	-1.19	-3	-1.02	-1.82	3.85	-0.88	0.34	-9.38	-8.65	-1.95	-0.58	1.2	2.29	0.04	8.06	4.77	0.74	-2.1	-0.49	-4.25	5.35	-3.8
GW042	-1.45	-3.3	-0.29	-2.29	2.02	-0.12	0.1	-4.78	-5.37	-0.36	2.05	0.72	1.16	-0.31	6.75	3.32	0.5	-0.5	-0.74	-1.46	7.98	-5
C3 Samples																						
GW025	-2.12	-3.4	-0.33	-2.36	2.22	-0.19	0.02	-7.24	-7.21	-0.56		0.96	0.85	-1.06	6.5	3.64	0.41		-0.81	-3.43		-2.1
GW044	-2.13	-3.8	-0.97	-0.46	2.65	-0.82	0	-9.47	-8.81	-1.5	-0.43	1.23	0.97	-1.37	6.72	4.16	0.4	-1.6	-0.83	-5.09	5.51	-1.8
GW012	-2.37	-3.9	-0.48	-1.27	1.14	-0.34	-0.3	-7.99	-7.79	-0.82	-0.51	1	-0.28	-2.13	5.49	3.07	0.09	-1.5	-1.12	-4.63	6.55	-2.5
GW061	-2.04	-4.2	-1.15	-0.71	2.35	-1	0.11	-9.33	-8.38	-1.54	-1.15	0.96	0.92	-0.99	6.54	3.81	0.51	-2.1	-0.73	-4.44	4.78	-2
GW021	-1.51	-2.6	-0.35	-0.11	3.18	-0.21	-0.07	-6.07	-7.19	-0.3	-0.81	1.53	1.52	-1.33	7.36	4.6	0.32	-2.1	-0.9	-3.62	5.21	-2
GW007	-1.91	-3.9	-1.18	-0.8	2.58	-1.04	0.02	-9.34	-8.73	-1.82	-0.55	1.19	0.9	-1.39	6.61	4.09	0.41	-1.9	-0.81	-4.96	5.44	-2.3
GW060	-2.2	-5	-1.93	-0.88	2.23	-1.78	0.04	-13.04	-10.71	-3.18	-1.77	1.05	0.53	-1.42	6.29	3.88	0.45	-2.8	-0.79	-6.91	4.13	-2.4
GW045	-4.08	-8.3	-1.87	-1.47	-1.63	-1.73	0.09	-17.21	-11.15	-3.28	-1.33	-0.68	-3.56	-3.39	0.87	0.51	0.49	-2.2	-0.74	-7.24	4.61	-2.2
GW062	-1.59	-2.8	-0.75	-0.73	3.5	-0.61	0.05	-9.13	-8.96	-1.49	0.09	1.54	1.9	-0.77	7.92	4.85	0.45	-1.3	-0.79	-5.16	6.02	-2.1
GW046	-2.71	-4.2	-0.72	-0.48	1.78	-0.58	-0.08	-9.89	-8.79	-1.21	0.56	0.98	-0.03	-2.08	5.49	3.47	0.32	-0.8	-0.92	-5.24	6.51	-2.3
GW020	-2.07	-2.7	-0.43	-0.44	2.72	-0.28	-0.13	-5.23	-6.58	-0.46	0.52	1.41	1.77	-0.49	7.96	4.23	0.26	-1.5	-0.96	-3.1	6.53	-2.5
GW028	-1.77	-3.3	-0.38	-2.19	2.65	-0.24	0.04	-7.39	-7.48	-0.52		1.13	0.97	-1.35	6.53	4.02	0.44		-0.79	-3.65		-2.2
GW034	-2.18	-4	-0.31	-2.29	1.58	-0.17	-0.07	-7.85	-7.41	-0.42	0.07	0.83	-0.02	-1.89	5.39	3.21	0.33	-1.5	-0.9	-3.81	6.04	-2.4
GW037	-2.67	-4.4	-0.28	-2.21	1.11	-0.14	-0.03	-8	-7.17	-0.35		0.57	-0.49	-2.06	4.71	2.76	0.37		-0.86	-3.51		-2.2
GW032	-2.81	-5	-0.46	-1.38	-0.45	-0.32	-0.07	-9.57	-7.93	-0.68		0.37	-1.34	-2.68	3.68	2.27	0.32		-0.9	-4.32		-2.3
GW039	-2.99	-4.3	-0.45	-0.04	0.96	-0.31	-0.36	-8.91	-8.38	-0.64		1.04	-0.69	-2.69	5.01	3.03	0.03		-1.19	-5.35		-2

Table 4.1: Saturation indices of possible reactive mineral phases in the groundwater and lake water samples from the study area (contd.)

C4	Anor	Arago	Ca-	Chalce	Chryso	Dolo	Fe	Gibbs	K-	Kaoli	Side	Goeth	Gyp										
Samples	Albite	thite	nite	Barite	rillonite	Calcite	dony	Chlorite	tile	mite	(OH)3(a)	ite	illite	Feldspar	k-Mica	nite	Qtz	rite	Silica (a)	Talc	ite	sum	
LWB37.5	-1.85	-4.7	0.77	-2.4	-2.59	0.91	-0.25	7.1	3.6	2.49		-0.89	-1.46	-0.49	3.35	-0.6	0.15		-1.08	6.83			-4.8
LWB15 Al	-1.81	-4.5	0.79	-2.36	-2.43	0.93	-0.27	7.29	3.58	2.52	1.17	-0.79	-1.31	-0.46	3.59	-0.5	0.13	-4.4	-1.1	6.77	7.15		-4.7
LWB25 Es	-1.67	-4.3	0.72	-2.44	-1.9	0.86	-0.25	6.71	2.97	2.36	1.01	-0.57	-0.88	0.31	4.17	0.03	0.14	-4.4	-1.09	6.2	6.98		-4.8
LWB8 Ad	-1.74	-4.3	0.89	-2.56	-2.43	1.03	-0.28	8.34	4.2	2.72	0.71	-0.78	-1.22	-0.38	3.68	-0.5	0.11	-5.1	-1.11	7.36	6.69		-4.9
LWB15 Al	-1.8	-4.4	0.91	-2.38	-2.53	1.05	-0.28	8.12	4.12	2.73	0.9	-0.83	-1.35	-0.45	3.52	-0.5	0.12	-4.9	-1.11	7.29	6.88		-4.7
LWB16 Al	-3.34	-5.4	0.12	-2.78	-2.63	0.27	-0.61	0.63	-1.13	1.11	0.96	-0.25	-2.15	-1.86	3.27	-0	-0.21	-3.5	-1.44	1.38	6.94		-5
LWC 75	-2.09	-4.5	0.69	-2.45	-2.31	0.83	-0.37	6.09	2.58	2.26	1.05	-0.56	-1.33	-0.74	2.76	-0.2	0.03	-4.4	-1.21	5.56	7		-4.8

The groundwater thus comprises direct rainfall that has been influenced by the mineralogy of the underlying rocks. Isolated cases of elevated chloride concentration are seen in two groundwater samples. These samples are thus classified as Na-Cl types (Fig. 4.5) and may indicate point sources of contamination.

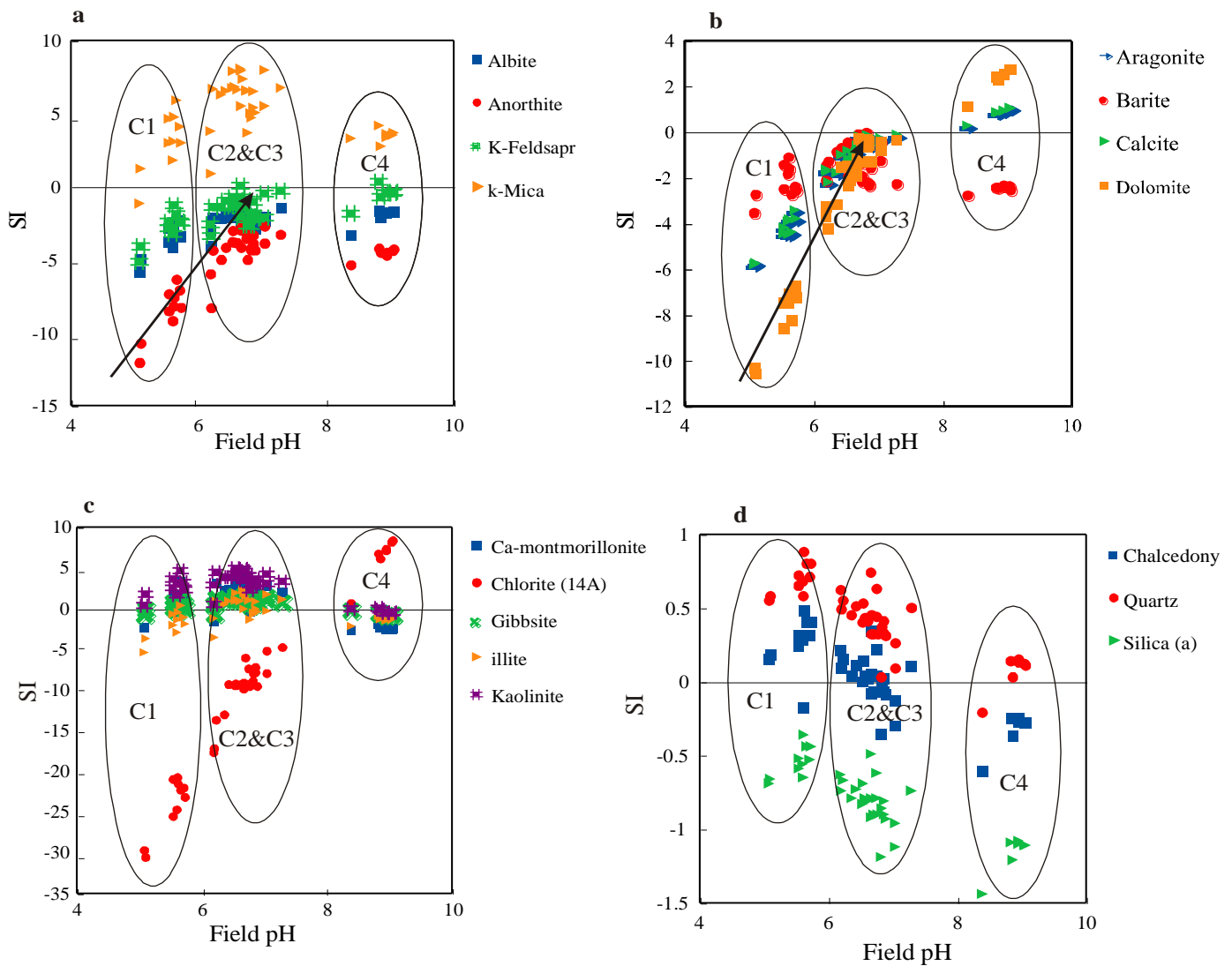


Fig. 4.6: Plots of saturation indices (SIs) with respect to various phases versus field pH for both groundwater and lake water. Arrows show that the groundwater approach equilibrium with increasing pH.

In general, the groundwater of the area increases in total ionic concentrations with a corresponding increase in pH from the upper catchment (C1 samples) towards the lower reaches (C3), and the cationic dominance shifts from sodium to calcium as depicted by the clusters (Figs. 4.4 and 4.5). This probably signifies the weathering of carbonates i.e. calcite, ankerite, Mg-calcite and dolomite in the underlying rocks. It is also possible that dissolution of other silicates (probably hornblende) or the selective leaching of calcium from anorthite in the rocks of the area or exchange of Ca^{2+} and Mg^{2+} on clay by aqueous Na^+ (Siegel and Pfannkuch, 1984). The high degree of spatial and statistical uniformity seems to suggest hydrochemical importance to the statistically derived clusters and the changes between these hydrochemical clusters symbolize the hydrochemical evolution of the groundwater around the Bosumtwi impact crater. Saturation indices of possible reactive mineral phases (Table 4.1) show that groundwater (C1-C3) is mostly undersaturated to saturated relative to albite, anorthite, aragonite, barite, calcite, chlorite, chrysotile, dolomite, gypsum, K-feldspar and talc at most locations.

Undersaturation and the trend towards equilibrium (from C1 to C3 samples) with respect to the primary silicate phases (e.g. albite, anorthite, and k-feldspar) and the carbonates (e.g. aragonite, calcite and dolomite) as pH increases (Fig. 4.6 a, b) further lend credence to the active weathering and evolution of the groundwater in the area. The trend observed in the generally low salinity (depicted by low TDS) groundwater of the area depicts a relationship of groundwater movement with lithology and topography, consequently showing a high degree of hydrochemical evolution corroborating the results of the Q-mode HCA.

TDS values for both groundwater and lake water are less than 1000 mg/l. Therefore both lake water and groundwater are fresh. A cross plot of TDS versus total hardness (TH) (Fig. 4.7) puts

C1 samples in the soft to moderately hard fresh water category; C2 samples fall largely in the hard fresh water zone while C3 and C4 are located in the very hard fresh water domain. These categories of hardness are temporary and can be removed by boiling (Driscoll, 1989).

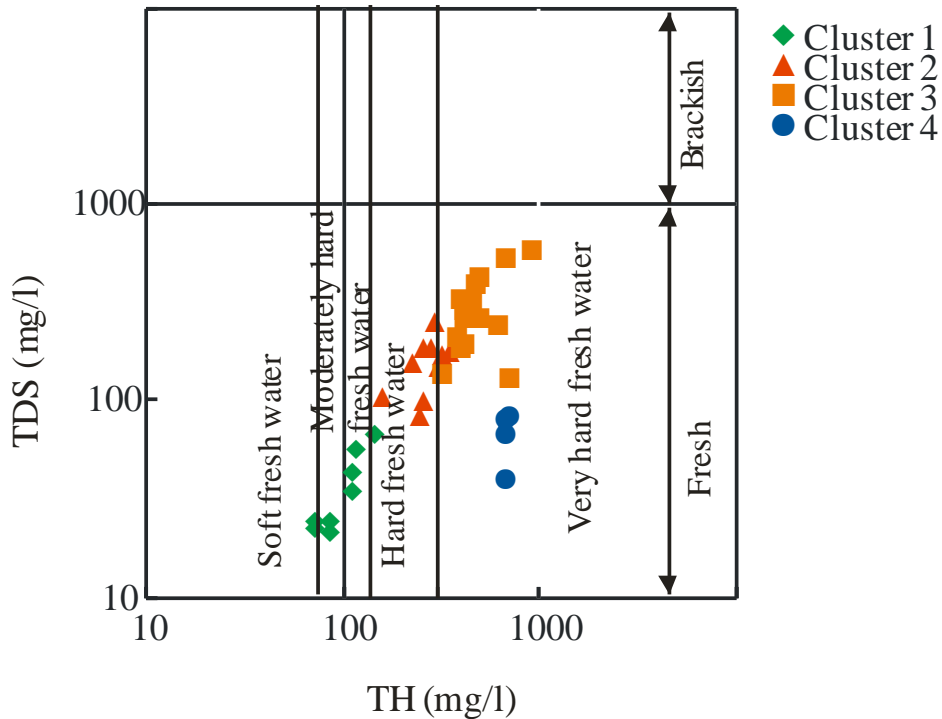


Fig. 4.7: Scatter plot of TDS vrs TH showing the quality of the water based on TDS and TH

4.3.1 Controls on groundwater and lake water hydrochemistry

Principal component analysis (PCA) of the physical and chemical dataset ranked the main factors controlling the hydrochemistry of the water bodies into three principal components (PCs) (Table 4.2a). A meaningful analysis requires that all variables/parameters included in the analyses make significant contribution to the final model. The significance of a

variable/parameter in the analyses was verified by its communality. A communality of 0.5 was set as the threshold, below which a variable is considered insignificant to the factor model. The communalities of all the variables used in this study are greater than 0.5 (Table 4.2b) hence each parameter makes very significant contribution to the model.

The PCs extracted explained 84% of the total variance in the hydrochemistry of the area (Table 4.2c). PC 1 explained as much as 42.78% of the variance and loads positively for EC, pH, K⁺,

Table 4.2: Results of R-mode factor analyses which presents a) Factor loadings of the final factor model after varimax rotation; b) Communalities of parameters; c) Variance explained by the factors in the factor model

a. Rotated Component Matrix												
PCs	pH	EC	K ⁺	Mg ²⁺	Ca ²⁺	Na ⁺	Si	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻
PC 1	.859	.815	.789	.323	-.001	.925	-.816	.325	.912	-.110	.019	.730
PC 2	.072	.536	-.207	.853	.940	.138	-.133	.171	.072	.331	.813	.554
PC 3	.434	.095	.340	-.214	.255	.089	-.132	.762	-.034	-.790	-.392	.305

b. Communalities												
	pH	EC	K ⁺	Mg ²⁺	Ca ²⁺	Na ⁺	Si	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻
Initial	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Extraction	.931	.961	.781	.877	.948	.882	.701	.716	.838	.746	.816	.933

c. Total Variance Explained									
Component	Initial Eigenvalues			Extraction Sums of Squared			Rotation Sums of Squared		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.121	51.012	51.012	6.121	51.012	51.012	5.134	42.782	42.782
2	2.852	23.766	74.778	2.852	23.766	74.778	3.094	25.784	68.567
3	1.158	9.649	84.427	1.158	9.649	84.427	1.903	15.860	84.427
4	.641	5.344	89.771						
5	.375	3.129	92.900						
6	.305	2.540	95.440						
7	.214	1.782	97.223						
8	.155	1.294	98.517						
9	.089	.745	99.262						
10	.047	.395	99.658						
11	.028	.236	99.894						
12	.013	.106	100.000						

Na^+ , Cl^- , HCO_3^- with a high negative loading for SiO_2 . It can be inferred from the results of the PCA (Table 4.2a), HCA (Fig. 4.2) and stiff diagram (Fig. 4.4) that C1 and C4 samples are largely described by PC1. This seeks to suggest that the major geochemical processes influencing the hydrochemistry of the study area generate the ions listed under PC1. PC1 also represents a process that retards the generation of silica in the system. Ratios calculated among the major ions from the arithmetic means of each cluster using Aquachem 4.0 suggest mineral weathering as a vital geochemical process that controls the concentration of ions in the waters. Briefly, the ratio between Na^+ and $(\text{Na}^+ + \text{Cl}^-)$ should be approximately 0.5 if Na^+ in groundwater is a result of halite dissolution, sea spray or brines (Kortatsi, 2004). However the average $\text{Na}^+ / (\text{Na}^+ + \text{Cl}^-)$ ratio of each cluster is greater than 0.5 suggesting sodium sources other than the dissolution of halite. Moreover halite has not been identified in the rocks within the area. This process probably signifies weathering and dissolution of silicates during initial infiltration and circulation of fresh recharging rainfall rich in CO_2 . Also, a binary plot of total cations (TZ) against $(\text{Na}^+ + \text{K}^+)$ (Fig. 4.8a) illustrates that all data points but the lake water (C4) plot near the $\text{Na}^+ + \text{K}^+ = 0.5\text{TZ}$ line, an indication that sodium and potassium ions in the groundwater are mainly the result of silicate mineral weathering, especially from the soda and potash feldspar that make up the rocks of the area (Karikari et al., 2007). Garrels and Mackenzie (1967) demonstrated that feldspar-rich igneous rocks are usually leached of cations and silica when infiltrated by aggressive recharge waters rich in CO_2 , thus, the relatively high values of silica (8.1 – 52.0) mg/l in the groundwater samples. Though Fig. 4.6d shows saturation to supersaturation with regard to quartz and undersaturation to supersaturation w.r.t. chalcedony (SiO_2), dissolved silica content in the groundwater is attributed to dissolution of silicate minerals

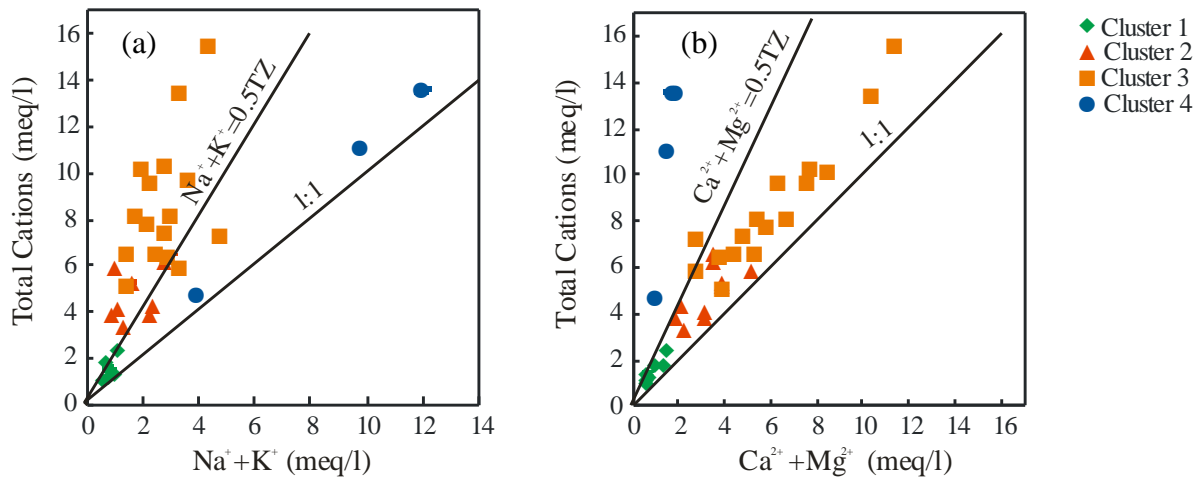


Fig. 4.8: Scatter diagram showing the relationship between a) TZ and $\text{Na}^+ + \text{K}^+$ and b) TZ and $\text{Ca}^{2+} + \text{Mg}^{2+}$

(plagioclase, alkali feldspars, biotite, muscovite) rather than quartz and chalcedony in the underlying rocks. This is because the latter are kinetically unreactive at low temperatures and rarely precipitates or dissolves at any significant rate (Freeze and Cherry, 1979). Silicate stability diagrams of Na, and Ca-aluminosilicate systems (Fig. 4.9) and saturation indices of reactive minerals phases (Table 4.1) support the interpretations of dissolution of aluminosilicates as the major geochemical process controlling the composition of the groundwaters and lake water of the BIC. Figure 4.9 shows that the groundwater samples plot within the kaolinite field. Stability of the groundwaters in the kaolinite field implies that the groundwater is probably at the intermediate stage of its evolution (Freeze and Cherry, 1979; Appelo and Postma, 2005) and discharging from silicates in semi arid region (Tardy, 1971). Undersaturation of the primary mineral phases (Table 4.1) could suggest slow dissolution kinetics or short residence time to allow adequate rock-water interactions and active dissolution of these minerals might be ongoing. The initial response in the weathering process of feldspar-rich rocks infiltrated by

aggressive recharge waters rich in CO_2 leads to the formation of gibbsite (Stumm and Morgan, 1996), however, the stability of C1 samples in the kaolinite field probably suggest that the amount of silica released to these samples is sufficient to convert the gibbsite to kaolinite

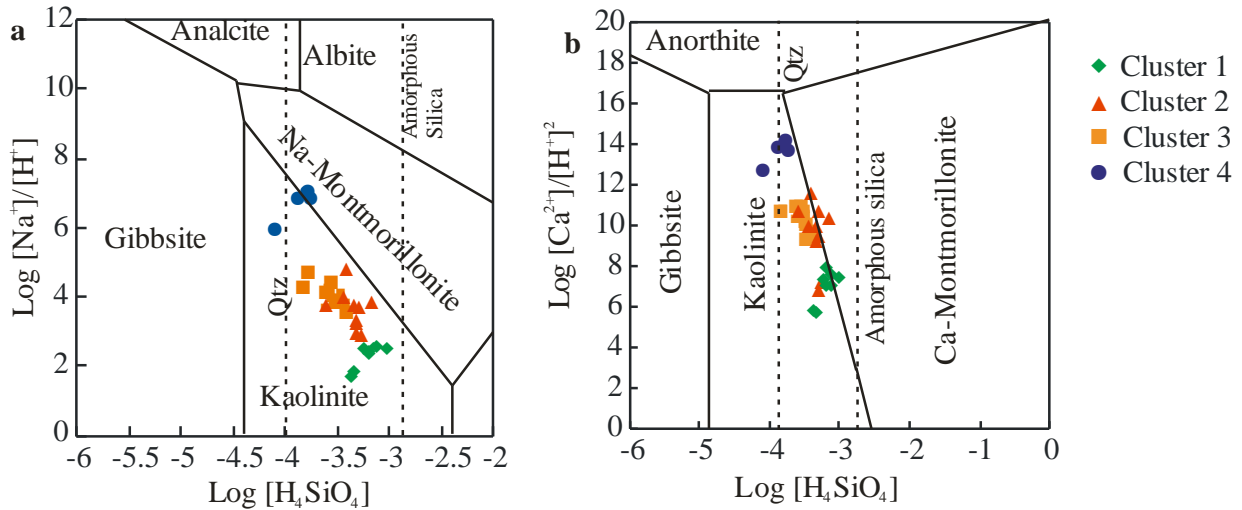


Fig. 4.9: Stability diagrams in (a) $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$, (b) $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ systems.

(Stumm and Morgan, 1996) hence the supersaturation of C1 groundwater with respect to kaolinite (Fig. 4.6c). As the groundwater evolves along flow path to C2 and C3 waters, the kaolinite probably reacts with more silica, consequently, the groundwater is supersaturated with Ca-montmorillonite at most locations (Fig. 4.6c) and the SiO_2 content is reduced. This is evident in Fig. 4.6d as the groundwaters steadily become undersaturated with regard to silica thus substantiates the negative loading of silica under PC1. It could also be possible that other clay minerals form in the system to consume silica. C2 and C3 samples remain in equilibrium with kaolinite (Fig. 4.9) due to the diminishment in the SiO_2 content of the groundwaters although the concentrations of cations increase (Fig. 4.9) along flow paths.

The lake water samples (C4) are more mineralized and deviate from the $\text{Na}^+ + \text{K}^+ = 0.5\text{TZ}$ line exhibiting higher $\text{Na}^+ + \text{K}^+$ concentrations (Fig. 4.8a). The increased mineralization of C4 is attributed to increased concentrations of Na^+ , K^+ , HCO_3^- and Cl^- ions which are magnitudes higher than those of C1 (Fig. 4.4) and most probably shows effect of evaporative enrichment, mineral precipitation or cation exchange activities (i.e. $\text{Ca}^{2+} + \text{Mg}^{2+}$ for bound Na^+) (Garrels and Mackenzie, 1967) in the lake water. Kortatsi (2007) also noted that other processes that can lead to Na-HCO_3^- types of water as observed for the lake include anaerobic degradation of organic matter and proton exchange. An equivalent bivariate plot of $(\text{Ca}^{2+} + \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-)$ and $(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$ (Fig. 4.10) was made to evaluate the significance of cation exchange activities in the hydrochemistry of the water bodies. If cation exchange activity is occurring between $\text{Ca}^{2+} + \text{Mg}^{2+}$ and $\text{Na}^+ + \text{K}^+$ then the slope of the scatter diagram should be -1 (i.e. $y = -x$) (Jankowski et al., 1998), however, Fig. 4.10 does not suggest any such relationship. It is therefore possible that evaporation and anaerobic degradation of organic matter may be contributing to the lake water chemistry since the area is forested with a prevailing semi-arid climatic condition. The evaporative effect in the hydrochemistry of the lake is seen by the supersaturation of the carbonates (Fig. 4.6b), which may lead to their precipitation thus limiting the concentration of Ca^{2+} and Mg^{2+} in the lake water (Fig. 4.4). Garrels and Mackenzie (1967) noted that in the process where evaporation causes the bivalent ions to form insoluble carbonates, the univalent ions alternatively concentrate continuously with a concomitant increase in HCO_3^- and pH. This observation is consistent with Lake Bosumtwi. The lake water alternatively is in equilibrium with kaolinite (Fig. 4.9b) and straddles the kaolinite - Na-montmorillonite boundary (Fig. 4.9a).

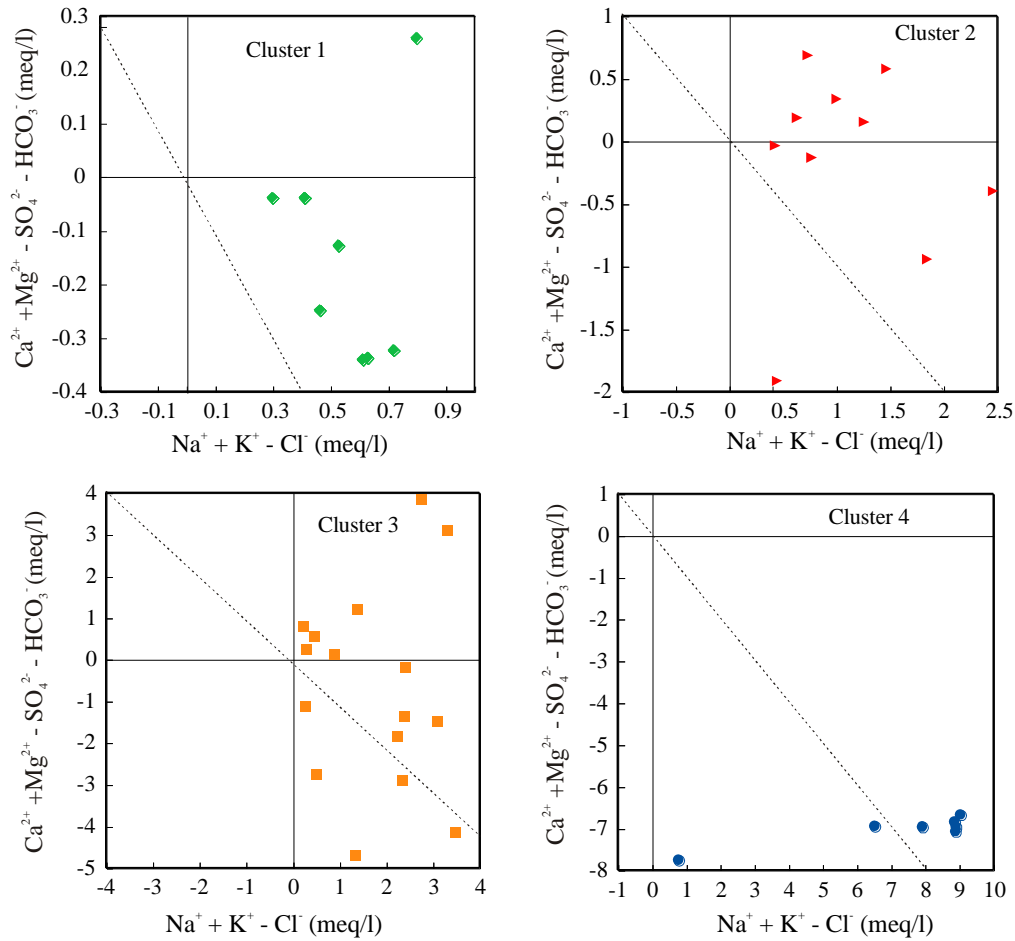


Fig. 4.10: Bivariate plots of $(\text{Ca}^{2+} + \text{Mg}^{2+} - \text{SO}_4^{2-} - \text{HCO}_3^-)$ vrs $(\text{Na}^+ + \text{K}^+ - \text{Cl}^-)$ (meq/l) for all cluster samples

Garrels (1984) demonstrated that where the concentration of sodium is high due to precipitation of calcite, cation exchange and the higher mobility of Na relative to Ca, Na-montmorillonite tends to be the most stable solid phase. The supersaturation of the lake water with respect to the carbonates (Fig. 4.6b) could lead to precipitation of calcite from the lake water hence the stability of the lake water in the Na-montmorillonite field of the Na^+/H^+ stability diagram (Fig. 4.9a).

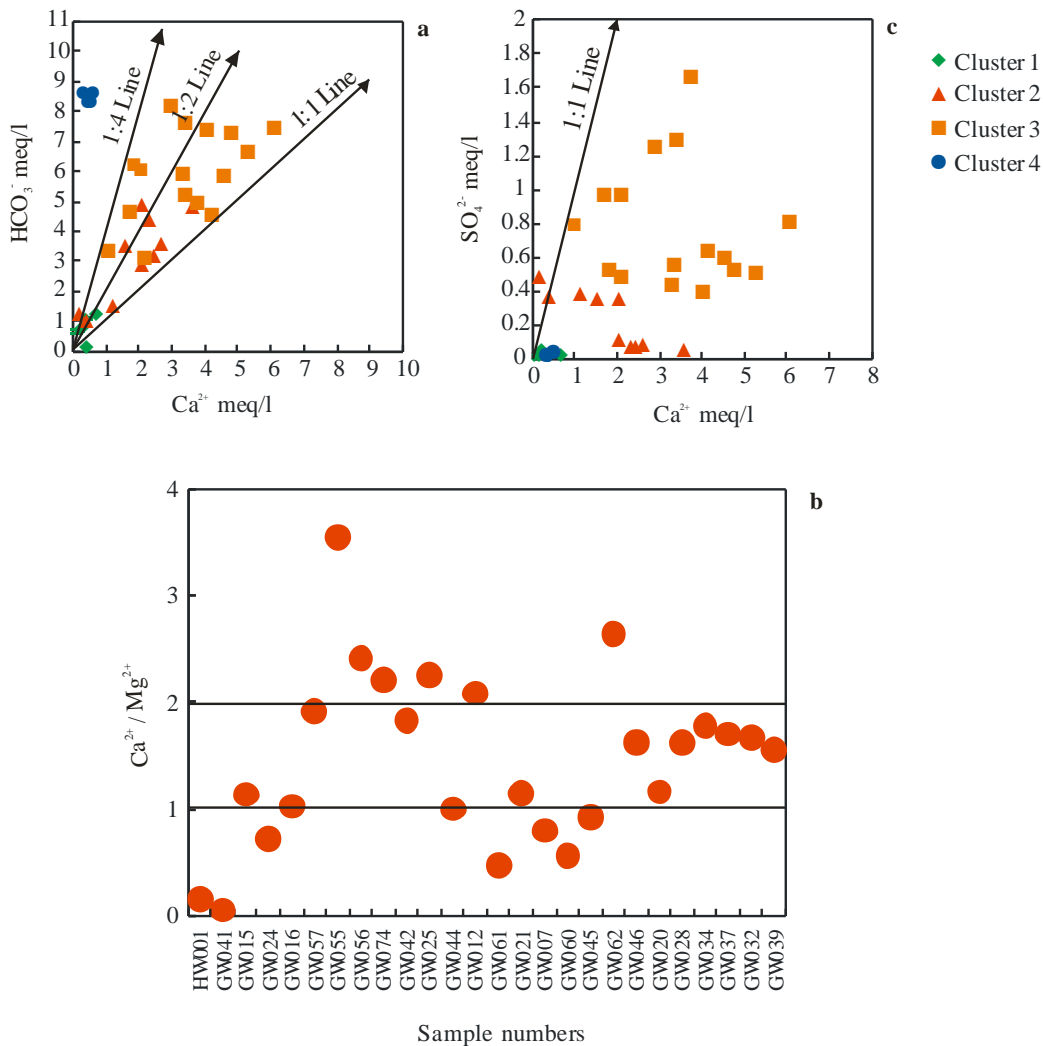


Fig. 4.11: Scatter diagram showing the relationship between a) $\text{Ca}^{2+} + \text{Mg}^{2+}$ and $\text{HCO}_3^- + \text{SO}_4^{2-}$; b) Ca^{2+} and HCO_3^- ; c) Ca^{2+} and SO_4^{2-} all in meq/l in the study area.

The second most important process in the hydrochemistry of the groundwater (PC2) accounts for 25.78% of the total variance and loads highly for EC, Ca^{2+} , Mg^{2+} , SO_4^{2-} and HCO_3^- . This process is typical of C2 and C3 groundwater samples in the study area. Ca^{2+} and Mg^{2+} ions were found to dominate the cations in these clusters. The presence and weathering of carbonate

minerals (calcite, ankerite, Mg-calcite and dolomite) (Karikari et al., 2007) play variable roles in the chemistry of groundwater from the study area. Garrels and Mackenzie (1967) demonstrated a 1:2 relationship between Ca^{2+} and HCO_3^- where calcite is dissolving and a 1:4 for the weathering of dolomite in the presence of carbonic acid. In the same way, where Ca^{2+} and SO_4^{2-} in the groundwater are derived from weathering of gypsum or anhydrite, an approximate ratio of 1:1 should exist between calcium and sulphate ions (Subramani et al., 2010; Yidana and Yidana, 2010). Ca^{2+} versus HCO_3^- plot (Fig. 4.11a) was made to verify the significance of CO_2 charged meteoric water in the weathering of carbonates, silicates and opaque minerals (sulphides) in the area. In this figure, some C1 and almost all C2 and C3 sample points fall between 1:4 and 1:1 lines and around the 1:2 line suggesting that the dissolution of calcite may be contributing cations (Ca^{2+}) to the hydrochemistry of the water. Further, it is evident from figure 4.11b that calcium and magnesium ions in clusters C2 and C3 samples probably result from the dissolution of calcite and dolomite. Dissolution of dolomite occurs when $\text{Ca}^{2+} / \text{Mg}^{2+}$ ratio is one whereas a ratio greater than one suggest contribution from calcite. Silicate mineral dissolution is apparent in cases where the $\text{Ca}^{2+} / \text{Mg}^{2+}$ ratio is greater than two. Thus carbonate mineral dissolution is the second most important process in the hydrochemistry of the groundwater.

The lake water (C4) and some C1 samples plot above the 1:4 line (Fig. 4.11a), however a scatter diagram of Ca^{2+} and SO_4^{2-} (Fig. 4.11c) does not suggest dissolution of gypsum or anhydrite and most samples exhibit excess Ca^{2+} over SO_4^{2-} indicative of other geochemical processes. It is observed that EC and HCO_3^- load highly under both PC 1 and 2 (Table 4.2a). The loading of bicarbonate under both PCs is not unexpected since both silicate and carbonate mineral dissolutions produce HCO_3^- . Both geochemical processes also contribute to the EC of the water.

The third component (PC3) loads positively for F^- and negatively for NO_3^- and explains 15.86% of the total variance. Although the concentrations of both F^- and NO_3^- in the waters are within acceptable limit (WHO, 2011), it is apparent from the PCA that their presence forms an important process in the hydrochemistry of the water. Fluoride can be characteristic of water found in felsic igneous and metamorphic rocks and through the application of fertilizers. Human activities within the basin has increased tremendously over the past few years and nitrate in the water could result from animal manure, sewage, nitrate fertilizers, decaying organic matter, and nitrate in the soil zone. This process probably indicates the effects of anthropogenic activities contributing to F^- and NO_3^- in the water resources of the area.

Conclusions

The chemical character of groundwater in aquifers around the Bosumtwi impact crater (BIC) has been used to define hydrochemical evolutionary trends, on the basis of lithology and topography. The groundwater evolved from Na-Mg- HCO_3^- waters at the upper catchments to predominantly Ca-Mg rich cations HCO_3^- water types as the water moved to lower elevations within the crater. The study identified the dissolution of silicate minerals contributing significantly to the Na-Mg- HCO_3^- waters followed by the weathering of carbonates contributing Ca-Mg rich waters. Silicate stability diagrams of Na, and Ca, aluminosilicate systems and saturation indices of reactive minerals phases support the interpretations of incongruent dissolution of aluminosilicates as the major geochemical process controlling the composition of the groundwaters. The stability of the groundwaters in the kaolinite field implies that the groundwater is probably at the intermediate stage of its evolution. Carbonate mineral weathering has also been identified to play some role in the groundwater chemistry. However, this process is to a lower extent. The lake water on the

other hand is characterised by Na-HCO₃ water type. In addition to the incongruent dissolution of aluminosilicates, the hydrochemistry of the lake was has been influenced by evaporation and supersaturation of carbonates.

References

- Aghazadeh, N. and Mogaddam, A. A. 2010. Assessment of Groundwater Quality and its Suitability for Drinking and Agricultural Uses in the Oshnavieh Area, Northwest of Iran. *Journal of Environmental Protection*, 1(1), 30-40.
- Ako, A. A., Shimada, J., Hosono, T., Ichiyanagi, K., Nkeng, G. E., Fantong, W. Y., Eyong, G. E. and Roger, N. N. 2011. Evaluation of groundwater quality and its suitability for drinking, domestic, and agricultural uses in the Banana Plain (Mbanga, Njombe, Penja) of the Cameroon Volcanic Line. *Environ Geochem Health*, 33(6), 559-575.
- Appelo, C. A. J. and Postma, D., 2005. *Geochemistry, groundwater and pollution*. 2nd Edition ed.: Rotterdam, A.A. Balkema.
- Banoeng-Yakubo, B. K., 2000. *The Application of Remote Sensing and Geographical Information Systems to Hydrogeological studies in the Upper West Region, Ghana*. (PhD). University of Ghana.
- Berry, J. K., 1995. Spatial reasoning for effective GIS. . . *GIS World Book*. Colorado Fort Collins.

- Boamah, D. and Koeberl, C., 2002. Geochemistry of Soils from the Bosumtwi Impact Structure, Ghana, and Relationship to Radiometric Airborne Geophysical Data. *In*: Plado, J. and Pesonen, L. eds. *Impacts in Precambrian Shields*. Springer Berlin Heidelberg, 211-255.
- Busby, J. F., Plummer, L. N., Lee, R. W. and Hanshaw, B. B. 1991. *Geochemical evolution of water in the Madison Aquifer in parts of Montana, South Dakota, and Wyoming*. . U.S. Geological Survey
- Corp, I., 2011. IBM SPSS Statistics for Windows. 20 ed. Armonk, NY IBM Corp.
- Dai, Z. and Samper, J. 2004. Inverse problem of multicomponent reactive chemical transport in porous media: formulation and applications. *Water Resour Res*, 40(W07407).
- Driscoll, F. G., 1989. *Groundwater and Wells*. Second edition ed. St. Paul, Minnesota: Johnson Filtration System Inc.
- Field, A., 2005. *Discovering Statistics Using SPSS*. Second ed. London, Thousand Oaks, New Delhi: SAGE Publications.
- Freeze, A. R. and Cherry, J. A., 1979. *Groundwater*. New Jersey: Prentice-Hall.
- Garrels, R. M. 1984. Montmorillonite/Illite stability diagrams. *Clays and Clay Minerals*, 32(3), 161-166.
- Garrels, R. M. and Mackenzie, F. T. 1967. Origin of the chemical composition of some springs and lakes. *In*: Equilibrium concepts in natural-water chemistry. Advances in Chemistry Series, . *American Chemical Society*, (67), 222-242.

- Gerla, P. J. 1992. Pathline and Geochemical Evolution of Ground Water in a Regional Discharge area, Red River Valley, North Dakota. *Ground Water*, 30(5), 743-754.
- Gill, H. E., 1969. *A Groundwater Reconnaissance of The Republic of Ghana, With A Description of Geohydrolic Provinces. Contribution to The Hydrology of Africa and The Mediterranean. Region.* . U.S. Government Printing Office Washington, D.C.
- Guler, C., Thyne, G. D., McCray, J. E. and Turner, A. K. 2002. Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. *Hydrogeology Journal*, 10(4), 455-474.
- Helstrup, T., Jørgensen, N. O. and Banoeng-Yakubo, B. 2007. Investigation of hydrochemical characteristics of groundwater from the Cretaceous-Eocene limestone aquifer in southern Ghana and southern Togo using hierarchical cluster analysis. *Hydrogeology Journal*, 15(5), 977-989.
- Hirdes, W., Davis, D. W. and Eisenlohr, B. N. 1992. Reassessment of Proterozoic granitoid ages in Ghana on the bases of U/Pb zircon and monazite dating. *Precambrian Research*, 56, 89-96.
- Jankowski, J., Acworth, R. I. and Shekarforoush, S., Reverse ion-exchange in deeply weathered porphyritic dacite fractured aquifer system, Yass, New South Wales Australia. . ed. *Proc. 9th Int. Symp. Water- Rock Interaction*, , 30 March-3 April 1998 Taupo, New Zealand, 243-246.

- Jones, W. B. 1985. The origin of the Bosumtwi Crater, Ghana-A historical overview. *Proceedings of the Geological Association (London)*, 96, 275-284.
- Jones, W. B., Bacon, M. and Hastings, D. A. 1981. The Lake Bosumtwi impact crater, Ghana. *Geological Society of America Bulletin*, 92(6), 342.
- Judd, A. D. 1980. The use of cluster analysis in the derivation of geotechnical classifications. *Bull Assoc Eng Geol*, 17, 193-211.
- Kaiser, H. F. 1960. The application of electronic computers to factor analysis. *Educational and Psychological Measurement*, 20, 141-151.
- Kesse, G. O., 1985. *The mineral and rock resources of Ghana*. Boston: Rotterdam, A.A. Balkema.
- Koerberl, C. and Reimold, W. U. 2005. Bosumtwi Impact Crater, Ghana (West Africa): An Updated and Revised Geological Map, with Explanations. *Jahrbuch der Geologischen Bundesanstalt, Wien (Yearbook of Australian Geological Survey)*, 145, 31-70.
- Kuells, C., Adar, E. M. and Udluft, P. 2000. Resolving patterns of ground water flow by inverse hydrochemical modeling in a semiarid Kalahari basin. . *Tracers and Modeling in Hydrogeology*, 262, 447-451.
- Lecomte, K. L., Pasquini, A. I. and Depetris, P. J. 2005. Mineral weathering in a semiarid mountain river: its assessment through PHREEQC inverse modeling. *Aquatic Geochemistry*, 11(173-194).

- Leube, A., Hirdes, W., Mauer, R. and Kesse, G. O. 1990. The early Proterozoic Birimian Supergroup of Ghana and some aspects of its associated gold mineralization. *Precambrian Research*, 46, 139-165
- Locsey, K. L. and Cox, M. E. 2002. Hydrochemical variability as a tool for defining groundwater movement in a basalt aquifer: The Atherton Tablelands, North Queensland.
- Marfia, A. M., Krishnamurthy, R. V., Atekwana, E. A. and Panton, W. F. 2004. Isotopic and geochemical evolution of ground and surface waters in a karst dominated geological setting: a case study from Belize, Central America. *Applied Geochemistry*, 19(6), 937-946.
- Parkhurst, D. L. and Appelo, C. A. J., 1999. *User's guide to PHREEQC – a computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations*. . Denver, Colorado: USGS
- Reimold, W. U., Brandt, D. and Koeberl, C. 1998. Detailed structural analysis of the rim of a large, complex impact crater: Bosumtwi Crater, Ghana. *Geology*, 26, 543-546.
- Rummel, R. J., 1970. *Applied factor analysis*. . Evanston: Northwestern University Press.
- Salem, Z. E., Sakura, Y. and Aslam, M. A. M. 2004. The use of temperature, stable isotopes and water quality to determine the pattern and spatial extent of groundwater flow: Nagaoka area, Japan. *Hydrogeology Journal*, 12(5), 563-575.
- Siegel, D. I. and Pfannkuch, H. O. 1984. Silicate dissolution influence on Filson Creek chemistry, northeastern Minnesota. *Geological Society of America Bulletin*, 95(12), 1446.

- Stumm, W. and Morgan, J. J., 1996. *Aquatic chemistry-Chemical Equilibria and Rates in Natural Waters*. New York;John Wiley & Sons, Inc.
- Stetzenbach, K. J., Amano, M., Kreamer, D. K. and Hodge, V. F.1999. Using multivariate statistical analysis of groundwater major cations and trace element concentrations to evaluate groundwater flow. *Hydrological Processes*, 13, 2655-2673.
- Subramani, T., Rajmohan, N. and Elango, L. 2010. Groundwater geochemistry and identification of hydrogeochemical processes in a hard rock region, Southern India. *Environ Monit Assess*, 162(1-4), 123-137.
- Suk, H. and Lee, K.-K. 1999. Characterization of a ground water hydrochemical system through multivariate analysis: Clustering into ground water zones. *Ground Water*, 37(3), 358-366.
- Tardy, Y. 1971. Characterization of the principal weathering types by the geochemistry of waters from some European and African crystalline massifs. *Chem Geol*, 7(4), 253-271.
- Thyne, G., Güler, C. and Poeter, E. 2004. Sequential Analysis of Hydrochemical Data for Watershed Characterization. *Ground Water*, 42(5), 711–723.
- Van der Kemp, W. J. M., Appelo, C. A. J. and Walraevens, K. 2000. Inverse chemical modeling and radiocarbon dating of palaeogroundwaters: The Tertiary Ledo-Paniselian aquifer in Flanders, Belgium. *Water Resour Res*, 36, 1277-1287.
- WHO, 2011. *Guidelines for Drinking-water Quality* [online]. Geneva, Switzerland.: World Health Organization. Available from: (<http://www.who.int>) [Accessed 4th March 2013].

- Wurl, J. Giese, S., Fausto, O. and Chale, G.2003. Ground water quality research on Cozumel Island, State of Quintana Roo, Mexico. ed. *Proc. second international conference on saltwater intrusion and coastal aquifers - monitoring, modeling, and management,*, 2003 Merida, Mexico, 1-4.
- Yidana, S. M., Banoeng-Yakubo, B. and Sakyi, P. A. 2012. Identifying key processes in the hydrochemistry of a basin through the combined use of factor and regression models. *Journal of Earth System Science*, 121(2), 491-507.
- Yidana, S. M., Ophori, D. and Banoeng-Yakubo, B. 2008a. Hydrochemical evaluation of the voltaian system-The Afram Plains area, Ghana. *J Environ Manage*, 88, 697-707.
- Yidana, S. M., Ophori, D. and Banoeng-Yakubo, B. 2008b. A Multivariate Statistical Analysis of Surface Water Chemistry Data—The Ankobra Basin, Ghana *J Environ Manage*, 86(1), 80- 87.
- Yidana, S. M. and Yidana, A. 2010. Assessing water quality using water quality index and multivariate analysis. *Environmental Earth Sciences*, 59(7), 1461-1473.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Hydrochemical and stable isotope data of water in Lake Bosumtwi and groundwater in aquifers surrounding the lake have been evaluated using conventional graphical methods, multivariate and mass balance models. The study found that the boreholes yield water of good to excellent quality for human consumption. An evaluation of the suitability of both groundwater and lake water for irrigation purposes based on salinity, sodicity and residual sodium carbonate reveal that the groundwater in the area is generally suitable for irrigation. About 21% of groundwater samples have low salinity and low sodicity and are acceptable for irrigation of most crops and almost all soil types without destroying the hydraulic properties of the soil. 38% are of medium salinity and low sodicity with the remaining 41% in the high salinity and low sodicity category. The lake water has high salinity and high sodicity and is not suitable for irrigation. However, where it becomes necessary to use the lake water for irrigation, it should be used on salt tolerant crops and on soils that have very high permeability like sands. The use of this category of water for irrigation requires special soil and water management.

The results indicate that recharge to the aquifers occurs on the hill tops by direct infiltration of evaporated recent meteoric water through fractures in the unsaturated zone to the saturated zone. Evaporation rates in the range of 45-51% estimated for the initial rainwater that starts infiltration and subsequent percolation to replenish the aquifer does not influence the chemistry of the groundwater of the area and its mineralization is controlled by minerals of the host rocks. The

isotope data of the lake indicates considerable enrichment in relation to local meteoric water, and suggests evaporation rate of 82% from the open lake surface resulting in increased concentration of the univalent cations. The study also established that any hydraulic connection between the two reservoirs may not benefit the aquifers in the area, although the converse is likely. This finding is at variance with an earlier assumption that suggested lake water seepage to the boreholes in the immediate vicinity of the lake.

Groundwater in boreholes located at higher elevations are typically Na-Mg-HCO₃⁻ water types which evolve to Ca-Mg- and mixed cations HCO₃⁻ water types at the lower reaches. Isolated cases of elevated chloride concentration are seen in two groundwater samples. These samples are thus classified as Na-Cl types and may indicate point sources of contamination. The major geochemical process controlling the composition of both lake water and groundwater has been attributed to incongruent dissolution of aluminosilicates. The groundwaters are stable in the kaolinite field which implies that the groundwater is probably at the intermediate stage of its evolution. The study also found that the lake water is chemically and isotopically distinct from the groundwater thus cannot explain the hydrochemistry of groundwater in the area particularly those boreholes in close proximity to the lake.

5.2 Recommendations

On the basis of some observations and findings from this research, the following are recommendations made for further work.

- Considering the socio-economic and scientific value of Lake Bosumtwi, it is important that the Government and Local authorities collaborate to manage and coordinate current

developmental and other human activities within the lake basin so as to protect the water resources and develop the eco-tourism of the area in a sustainable manner.

- This study has shown that the groundwater quality is suitable for both domestic and irrigation use. It is, however, recommended that further work should be carried out within the basin to establish the potential of the groundwater to meet these needs of the people.
- Results from the work indicated that recharge probably occurs on top of the mountain and the water flows down gradient towards the lake. Further work should be carried out to provide additional information about the flow paths since this cannot be identified with certainty using the stable isotopes of oxygen and deuterium as water within the same flow path can be obtained from different sources. Also, the geochemical processes responsible for the consumption of silica along the flow path should be investigated. It is also recommended that the recharge areas should be identified and protected from activities that may in the future cause pollution of the groundwater systems in the area.
- The study also shows that any hydraulic connection between the two reservoirs may not benefit the aquifers in the area, although the converse is likely. It is also important that further work is conducted in order to establish and quantify with certainty groundwater discharge into the lake.
- Studies show that the lake bed is highly fractured (Danuor and Menyeh, 2007) and the fact that the Birimian rocks contain aquifers at deeper depths which have not been investigated by this study, it is important that the deeper aquifer are studied to determine if the lake water seeps into the latter of the area.

References

Danuor, S. K. and Menyeh, A. 2007. Results of pre-drilling potential field measurements at the Bosumtwi crater. *Meteoritics & Planetary Science*, 42(4-5), 541-547.