SOURCES AND HYDRO-GEOCHEMICAL CHARACTERISTICS OF LAKE DULUTI WATERS,TANZANIA

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ABSTRACT

Water chemistry, and stable isotopes of oxygen and hydrogen (^{18}O and ^{2}H), were used collectively to characterize and quantify Lake Duluti (L. Duluti) – groundwater interaction. Physico-chemical parameters including temperature, pH, electrical conductivity, dissolved oxygen, total dissolved solids, alkalinity, major cations and anions were used to determine chemical characteristics of the lake and to assess its relationship with groundwater sources. Furthermore, water balance approaches were used to estimate surrounding ground-water exchange with L. Duluti and addressing the role of groundwater on lake hydrological system. Physico-chemical parameters results showed abundance of major cations and anions in the lake water in the following order $Na^{+}>Ca^{2+>}K^{+}>Mg^{2+}$ and $HCO_3^{-}>Cl^{-}>F^{-}>SO_4^{2-}>NO_3^{-}$ respectivelly. Water in L. Duluti was found to be of predominantly Na-HCO_3 type while that from springs and boreholes was of the Ca-HCO_3 and Ca-Na-HCO_3-types, respectively. Isotopic results indicated that evaporation-induced isotopic enrichment prevailed in L. Duluti and contributed significantly to water loss from the lake. The isotopic composition of oxygen ($\delta^{18}O$) of lake water averaged sigma notation(‰) of 6.1 ‰ while that of well/boreles and spings averaged -1.2 ‰ and -2.1 ‰ respectively. Similarly, the isotopic composition of hydrogen (δD) of lake water averaged 24.2 ‰ while that of well/boreles and spings averaged -12.9 ‰ and -12.2 ‰ respectively. Stable isotope calculations suggested that L. Duluti loses water to the aquifer and it is more recharged by the groundwater relative to precipitation and surface runoff. Groundwater inflow to the lake is approximately 2 430 960 meter cubic per year (m^3/yr) while lake water discharge to groundwater is 2 902 620 m^3/yr. The lake is recharged through precipitation by 612 000 m^3/yr. Hence, groundwater plays a major role in the hydrological system of L. Duluti. Based on these findings from the study, there is more groundwater outflow than inflow, hence citing of boreholes in the area should be properly done so as to maintain the state of the lake or groundwater aquifers. In the long run, pumping water from the lake may also introduce more groundwater inflows and less outflows. The findings in this research are of assistance to policy makers and management personnel to make use of the information provided for better management of the lake water. The information will also enable the Arusha water supply and sewerage authority to know the hydrological state of L. Duluti.

DECLARATION

I, Nancy P. Mduma do hereby declare to the Senate of Nelson Mandela African Institution of Science and Technology that, this dissertation is my own original work and that it has neither been submitted nor being concurrently submitted for degree award in any other institution.

Name and signature of candidate **Date**

The above declaration is confirmed

Name and signature of supervisor 1 **Date**

Name and signature of supervisor 2 **Date**

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CERTIFICATION

This is to certify that the dissertation entitled *"Sources and Hydro-geochemical characteristics of Lake Duluti water"* submitted by Ms. Nancy P. Mduma (M223/T.13) in partial fulfilment of the requirements for the award of Master's in Hydrology and Water Resources Engineering at Nelson Mandela African Institution of Science and Technology, Tanzania is an authentic work carried out by her under my guidance.

Principle Supervisor	**Date**
Co-Supervisor	**Date**

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I am greatly indebted to Pangani Basin Water Authority, Duluti Forest Reserve Office, Wards and Village Executive Officers of Kikwe and Akheri, owners of boreholes for their cooperation during my fieldwork. Finally, I wish to thank Prof. Alfred Muzuka, Dr. Hans Komakech and Prof. Jing Zhang for their guidance during this study, which has enabled me to refine my research skills.

DEDICATION

I dedicate my work to my family. A special feeling of gratitude to my loving parents, Eng. Praygod Mduma and Anna Mapunjo whose words of encouragement and push for tenacity that gave me positive energy to carry out my research. Also, equally deserving a share of this dedication are my brothers Prince and Brian Mduma who have supported me throughout the entire process.

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LIST OF ABREVIATIONS ND SYMBOLS

Ca^{2+}	Calcium
Cl^-	Chloride
CO_3^{2-}	Carbonate
COD	Chemical Oxygen Demand
DEM	Digital Elevation Model
DO	Dissolved oxygen
EC	Electrical conductivity
F^-	Floride
GIS	Geographical Information System
GMWL	Global Meteoric Water Line
GPS	Geographic Position System
HCO_3^-	Bicarbonate
IAEA	International Atomic Energy Agency
K^+	Potasium
LMWL	Local Meteoric Water Line
m	Metre
MANOVA	Multi Analysis of Varience
Mg^{2+}	Magnesium
mg/l	milligram per litre
mm^3/yr	Milimeter cubic per year
m^3/yr	Meter cubic per year
Na^+	Sodium
NM-AIST	Nelson Mandela African Institution of Science and Technology
NO_3^-	Nitrate
SARI	Seliani Agricultural and Research Institute
SKLEC	State Key Laboratory of Estuarine and Coastal Research
SMOW	Standard Mean Ocean Water
SO_4^{2-}	Sulphate
TC/EA	High temperature convension elemental analyser
TDS	Total Dissolved solids
TMA	Tanzania Meteorological Agency
VSMOW	Vienna Standard Mean Ocean Water

$\delta^{18}O$	Stable isotopes of Oxygen
δD/ δH	Stable isotopes of Hydrogen
°C	Degree Celcius
%	Percentage
‰	Sigma notation in per mil

CHAPTER ONE

INTRODUCTION

1.1 Background information

All freshwater bodies including rivers and lakes constitute a valuable resource to the world. In Tanzania, more than 75% of the population depends on surface water (Kashaigili, 2012; Elisante & Muzuka, 2015). Exploitation of surface water is on the increase due to population increase and its associated consumption for domestic, industrial, agricultural, and other purposes/uses linked to improvement of standard of living. Quantity and quality of surface water in many parts of the world are threatened by natural and anthropogenic activities. In Tanzania, the quality and quantity of surface water are deteriorating due to human and natural activities (Elisante & Muzuka, 2015) and consequently threatening human health and environment in general. Due to such deterioration, a portion of the population uses groundwater as an alternative water source. Nevertheless, the hydrological part of surface and groundwater sources and their relations in many areas of Tanzania remain poorly understood. In order to conserve and utilize the valuable water resources effectively and be able to exploit it sustainably, it is important to consider hydrological systems, which implicitly make it essential to understand the hydro-geochemical characteristics of lake and groundwater sources (Kumar *et al*., 2006).

Various uses of water e.g. for domestic, irrigation or industrial purposes depend on its quality particularly physico-chemical and biological quality. Water quality and quantity are controlled by a number of factors, such as climate, geochemistry, duration of contact with rocks, topography of the area, saline water intrusion in coastal areas, human activities on the ground, etc., (Reghunath *et al.*, 2002; Hiscock, 2005; Ayenew, 2006; Martinez *et al.*, 2015). Apart from these factors, the interaction between surface water and adjacent groundwater and the mixing of different types of groundwater may also play important roles in determining quality of surface and groundwater (Darling *et al.*, 1996; Reghunath *et al.*, 2002).

Lake Duluti, a crater lake on the slopes of Mt. Meru, is a topographically closed freshwater body with no obvious surface inflow and outflow and therefore, assumed to receive and discharge its water through subsurface flow, precipitation and evaporation (Öberg *et al.*, 2012). Evaporation in closed lakes may result in accumulation of solutes (Belay, 2009; Mckenzie *et al.*, 2010; Öberg *et al.*, 2012), which may compromise its potential to be used for human consumption. According to (Öberg *et al.*, 2012), L. Duluti loses its solutes through subsurface flow. Fresh water lakes and aquifers are important water resources and are used extensively for various human activities such as agriculture, industrial and domestic consumption (Yihdego & Becht, 2013; Mulwa *et al.*, 2013). L. Duluti and surrounding aquifers are important water resources in the area and are used for irrigation and domestic water supplies. Additionally, there is a plan to use water from the lake in future as a source of water for Arusha city. Nevertheless, continued abstraction from the lake and the surrounding aquifers, which is on the increase, may have potentially negative impact on water levels and quality of these resources. Hydro-chemical data with other information such as water level, stable environmental isotopes can be used to ascertain the interaction between surface water and groundwater (Mckenzie *et al.*, 2010; Kamtchueng *et al.*, 2014; Martinez *et al.*, 2015). However, prior to this study, such information for L. Duluti was not available. The objectives of this study was to assess the source and water chemistry of L. Duluti.

1.2 Research problem and justification of study

The production capacity of the sources of water supply in Arusha city practically fluctuates seasonally from an average of 32 000 m^3/day in dry season to 60 000 m^3/day during the rainy season. Owing to increasing water demand as a result of population growth, economic development and climate change, the daily water demand is estimated to the tune of 53 030 m^3/day.

This underlines the fact that additional water sources are required in order to ensure adequate supply throughout the year including during dry seasons. L. Duluti has been identified as an alternative source of water supply needed to meet growing water demand in Arusha city. This is because the current water supply does not meet half the city’s demand especially during the dry season as rated above. However, lack of adequate knowledge on the hydrological system of the lake and its quality, exploitation of the water resources has not been possible. The source of lake water and chemical characteristis of the lake is poorly understood therefore, limiting the sustainable use of the lake water.

Been a crater lake, L. Duluti is assumed to be recharged by groundwater, and hence it is important to confirm and quantify lake-groundwater interaction so as to explore the impacts of abstraction of lake water e.g. the existance of the lake or groundwater aquifers. Sustainability of the L. Duluti will depend on on the understanding of its water sources as well as the effects of natural and anthropogenic activities around the lake. This study is an attempt to provide the information on the origin of the lake water, lake-groundwater interaction, and physico-chemical characteristic of water. Furthermore, the findings from this work are likely to support policy makers and water managers to make better decisions on the management of the lake water. The information will specifically enable the Pangani Basin Water Board and Arusha water supply and sewerage authority to make informed decision on sustainable use of L. Duluti water.

1.3 Objectives

1.3.1 General objective

The main objectives of the research work were to assess the sources and hydro chemical characteristics of Lake Duluti waters.

1.3.2 Specific objectives

(i) To ascertain chemical characteristics of water in Lake Duluti

(ii) To identify and quantify the source of water recharging the lake (Lake – groundwater relation)

1.4 Research hypothesis

(i) The lake is fed by groundwater and rain water

(ii) Chemical characteristics of Lake Duluti water is influenced by rainfall and sorrounding groundwater sources.

(iii) There is a positive water balance among various components recharging the lake.

1.5 Significance of the research

Conducting an estimate of L. Duluti water balance provides a comprehensive understanding of the water flow system and water resources in the study area. This study has addressed the role of groundwater, with a focus on quantifying the groundwater exchange with L. Duluti. The findings from this research will help to provide baseline information about the lake hydrological system for effective management of the lake. The results will be used as evaluation tools for management of lake water and reveals the effects of surrounding groundwater sources on the survival of the lake.

CHAPTER TWO

MATERIALS AND METHODS

2.1 Summary

This chapter describes methodology used on conducting the study. The study area is described based on its location, geology and climate. Furthermore, fieldwork and laboratory work for analysis of water samples are also explained in detail. Lastly, different analytical methods for the data obtained from field and laboratory are also discussed.

2.2 Description of the study area

2.2.1 Location

The study area, which include L. Duluti, and its surroundings, is located east of Arusha town, between latitude 3°21′S to 3°25′S and longitude 36°46′E to 36°49′E in northern Tanzania (Fig. 1). The lake is situated at an altitude of 1 290 m and has an estimated surface area of 0.6 km^2 and maximum depth of approximately 9 m (Öberg *et al.*, 2012). The catchment is confined by the crater walls with no surface inlets or outlets. Additionally, unlike many other crater lakes, L. Duluti water is reported to have low salinity (Öberg *et al.*, 2012), indicating a continuous exchange of water masses and loss of ions through the process.

2.2.2 Geology

Lake Duluti, a crater lake, is situated in one of the parasitic volcanoes that were associated with Mt. Meru eruptions. Geologically, L. Duluti has a crater rim primarily consisting of finely stratified ashes and tuffs. Elevated ridge to the north, east and west of the lake consists of weathered vesicular basalt. The lake and surrounding sampled areas are dominated by alkaline igneous rocks, mostly phonolites and nephelinites (Wilkinson *et al.*, 1983; Dawson, 1992; Öberg *et al.*, 2012) see Fig. 1 of the geology map of the study area, and that of sampled water points .

2.2.3 Climate

The dominant climate is tropical type with clearly defined rainy and dry seasons. Rainfall is bimodal with an annual average above 1 000 mm/year distributed mainly between two seasons namely, short rains of October/November to January and long rains of February/March to May (Öberg *et al.*, 2012; Meru District Council, 2013) as depicted in Fig. 2 of monthly rainfall data collected for 65 years from Tengeru Metrological station. The decrease and high variability of rainfall contributes to the demand of water for different activities taking place in the sorrounding areas of L. Duluti.

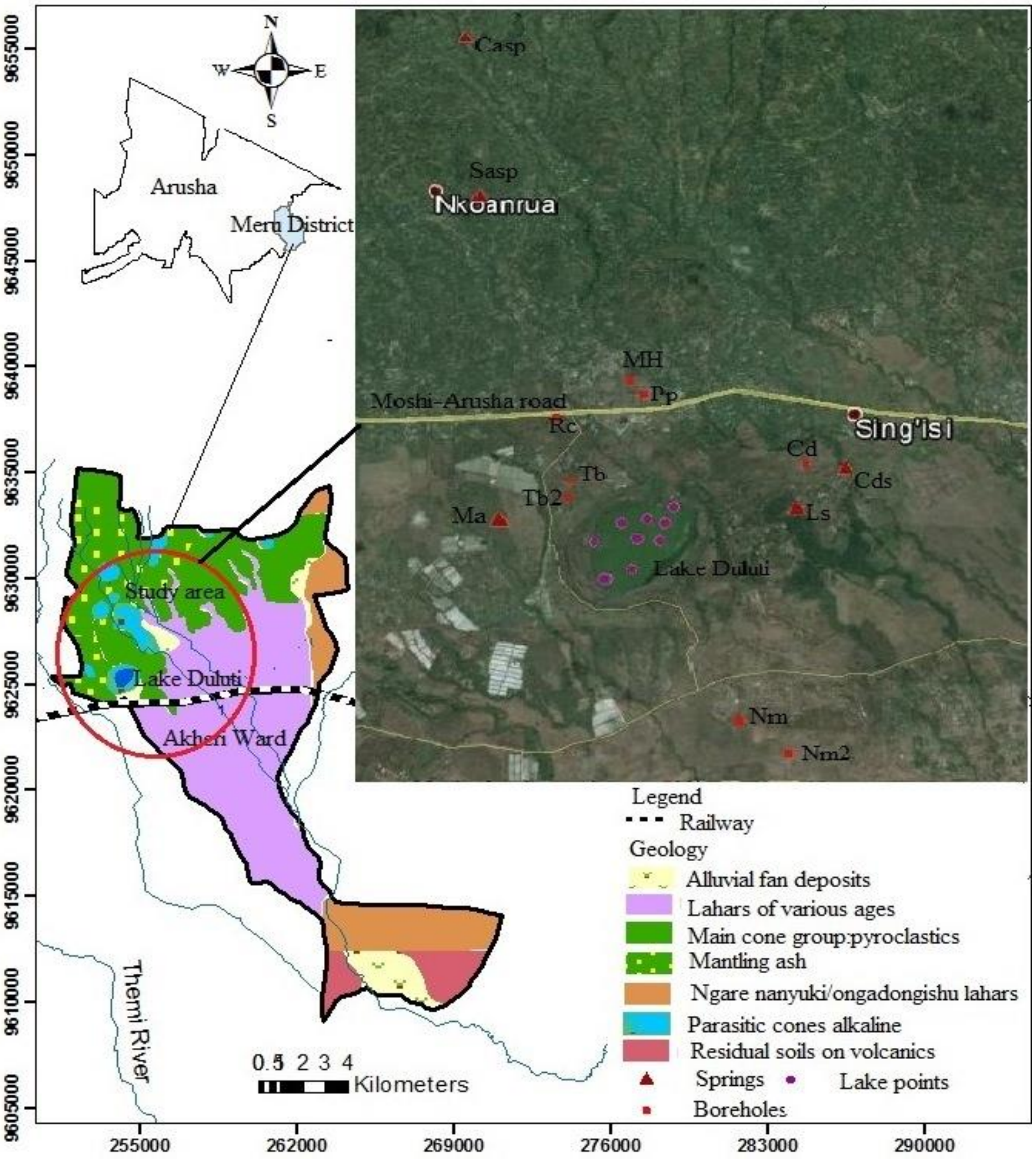


Figure 1: Study area showing the geology of the area and sampling site in L. Duluti and surrounding water sources

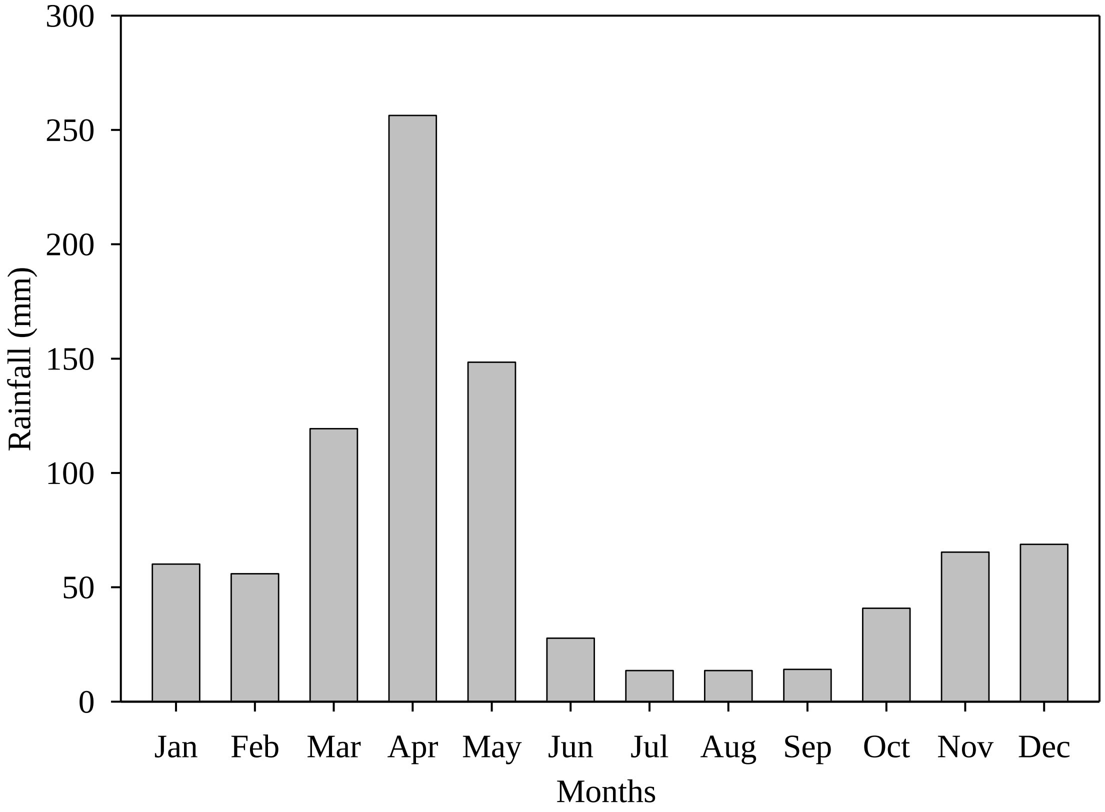


Figure 2: Average Monthly Rainfall variation from Tengeru Metrological station

2.2.4 Lake water levels

Monitoring data on L. Duluti exhibiting water levels are necessary for management of the lake. Lake Duluti water levels has been gauged for over 26 years, but some of the data are not available and hence creating a gap on the long trend of lake water level. Consecutive data for 12 years (2003 to 2014) for lake water level were obtained from Pangani basin water office. Lake Duluti water levels recorded for the mentioned number of years showed top water level having slight fluctuations through a range of about 1.5 metres.

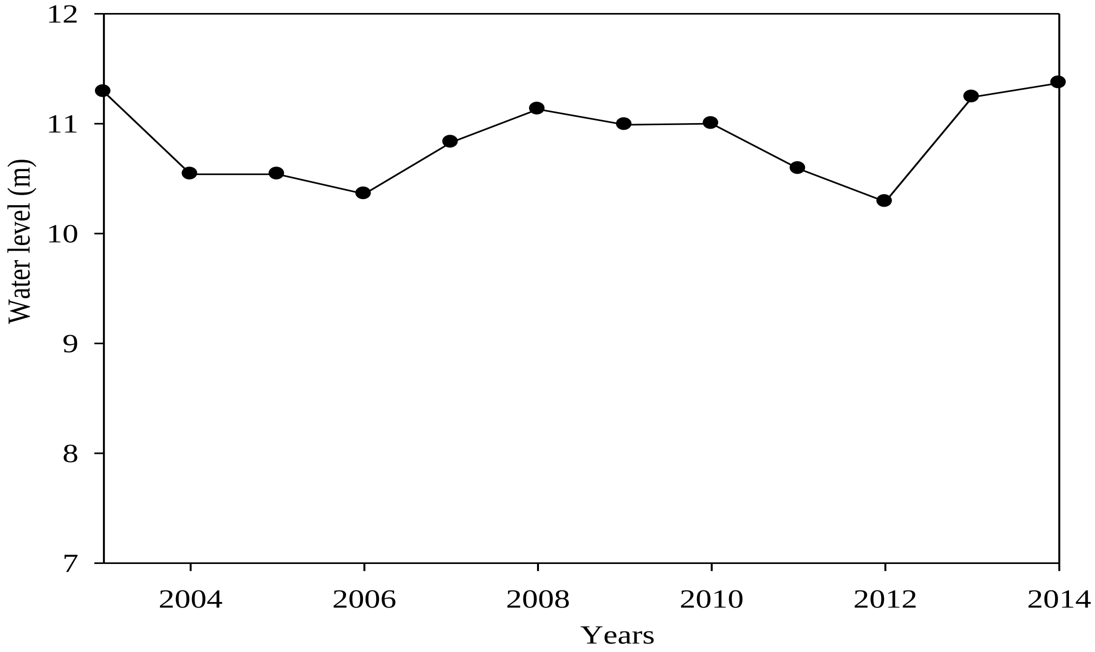


Figure 3: Lake water levels trend for a number of years

2.3 Methodology and laboratory work

2.3.1 Fieldwork

Fieldwork involved collection of water samples in pre-washed polyethylene bottles from L. Duluti and surrounding groundwater resources during dry (January-February 2015) and wet (March – April, 2015) seasons. During the water sampling exercise for determining chemical characteristics, each bottle was rinsed at least three times with the water to be collected before sampling. Dissolved oxygen (DO), pH, temperature, total dissolved solids (TDS) and electrical conductivity (EC) were measured on site using a multi-parameter meter. Water samples from L. Duluti were collected at ten sampling stations, and at different depths including surface and bottom using a water sampler.

Water samples from boreholes were collected after pumping to ensure substitution of stagnant water by freshwater from aquifer. Water samples were also collected from surrounding springs. Samples for cation analysis were acidified with nitric acid (Supra pure) onsite to $pH < 2$ to prevent precipitation of cations and water sample for nitrate were acidified with sulphuric acid to $pH<2$. Finally, samples were placed in clean ice boxes, and transported back to the laboratory where they were stored in the refrigerator until analysis. The geographic co-ordinates and altitude were also taken at each sampling location using a Geographic Positioning System (GPS).

Sampling of water from Lake Duluti and surrounding ground water sources during dry and wet seasons and at points/site mention above was carried out for isotope analysis. Water sampling was done as described above on sampling for chemical characteristics. However, in order to minimize isotopic fractionation resulting from evaporation, samples were kept in Amber glass bottles with Teflon-lined caps and stored in the refrigerator at at -4°C in the Nelson Mandela Afican Insitution of Science and Technology (NM-AIST) laboratory prior to analysis at State Key Laboratory of Estuarine and Coastal Research, China.

2.3.2 Laboratory work

Determiation of major cations (Ca^{2+}, Mg^{2+}) was done by titration, while K^+ was determined by using Chemical Oxygen Demand (COD) Multi-paremeter spectrophotometer (HANNA® 83099) at the NM-AIST water quality laboratory. Sodium was analyzed at Seliani Agricultural and Research Institute (SARI) by the Flame Photometer method. Major anions (CO_3^{2-}, HCO_3^-, Cl^-,) were determined by titrimetric method while $NO_3^-$and SO_4^{2-} were determined by COD Multi-parameter at NM-AIST water quality laboratory.

The stable isotopes compositions of oxygen and hydrogen were determined using High temperature conversion elemental analyzer-mass spectrometry (TC/EA-MS) by injecting 0.1 ml of the sample using a microliter syringe. Helium was used as carrier gas of the sample through a heated septum. H_2O samples were reduced by reaction with glassy carbon and vaporized at high temperature of 1400°C. All samples were measured at least four times and the final result was reported as mean value. The results are reported in **δ-** notation in per mil (‰) and reproducibility was better than 0.3 and 3‰ for $\delta^{18}O$ and δD, respectively.

2.4 Data analysis

Statistical tests were carried out using STATISTICA™ StatSoft 7.0. Average, standard deviation, maximum and minimum value were calculated for all parameters in dry and wet season. Multivariate analysis of variance was used to assess the effect of water sources on water chemistry while the interrelationships among different variables were assessed using correlation matrix.

CHAPTER THREE

HYDRO-CHEMICAL CHARACTERIZATION OF LAKE DULUTI AND GROUNDWATER SOURCES

3.1 Summary

Physico-chemical parameters including temperature, pH, electrical conductivity, dissolved oxygen, total dissolved solids, alkalinity, major cations and anions were used to determine chemical characteristics of Lake Duluti and to assess its relationship with groundwater sources. Water samples were collected from the Lake and selected groundwater sources including springs and boreholes during wet and dry seasons. Some of the physical parameters were measured in situ and some of them, chemical parameter were analysed in the laboratory. Results showed concentration of major cations and anions in the Lake water to be in the following order $Na^{+}>Ca^{2+}>K^{+}>Mg^{2+}$ and $HCO_3^{-}>Cl^{-}>F^{-}>SO_4^{2-}>NO_3^{-}$, respectively. Water in L. Duluti was found to be of predominantly Na-HCO_3 type while that from springs and boreholes was of the Ca-HCO_3 and Ca-Na-HCO_3 types, respectively. Water in L. Duluti was alkaline while that of surrounding groundwater sources was slightly acidic to slight alkaline. Electrical conductivity (EC) and Total dissolved solids (TDS) of the lake were low indicating its freshwater nature. Similarly, concentration of F^{-} averaged 3.1 milligram per litre (mg/l) in the Lake, probably a result of accumulation due to evapo-transpiration taking place in lake Duluti. Findings on the chemical characteristics together with the isotopes data in the next chapter will be used to confirm if there is interaction between the Lake and groundwater, which is influenced by different factors to be discussed. These results are important to managers and formulators of water policies for making informed decisions on management of the lake.

3.2 Introduction

The chemical composition of water determines the water's suitability for various human and ecosystem uses. It is a result of intrinsic capacity of water to dissolve chemical substances, the natural interaction of water with other spheres during hydrologic cycle and pollution due to human activities (Hiscock, 2005). The interaction of water with other spheres may result to processes such as sorption, biodegradation of dissolved substances, redox reactions, precipitation, co-precipitation and complexation of chemical substances in the groundwater consequently increasing or lowering levels of a particular chemical component above or below safe levels (Hiscock, 2005).

Hydrochemical study is a useful approach for identifying the suitability of the particular water resource. Physico-chemical parameters studied are important in the chemical characterization of lake water and that of the surrounding groundwater sources so as to evaluate the real contribution of the parameter as in relation to the particular water sources and their trend. The physical parameters taken into consideration in the present study includes temperature, color and odour while the chemical parameters are hydrogen ion concentration, total dissolved solids, specific conductance, total hardness and all major cations and anions. In this study, water sampling was done from Lake Duluti and surrounding boreholes and springs, concentration levels of some of the parameters for the sampled water sources were measured in-situ while others were analysed in the laboratory as described in the methodology part in chapter two.

The chemical composition of water offers an understanding of the origin, actual flow path and mixing of water. To understand the water chemistry it is important to identify hydro chemical facies and hydro geological processes that occur during water flow. Results are presented and discussed in the next section by showing concentration levels of each parameter and its variation with depth and water sources. Water types for the different water sources are also determined from the interaction of factors such as geological structure of the area and precipitation which also control the chemical composition of water. The purpose of this study is to determine the physic-chemical characteristics of Lake Duluti and groundwater sources in the study area and their relation.

3.3 Results

3.3.1 Physico-chemical characteristics of L. Duluti and surrounding groundwater sources

The physicochemical characteristics of L. Duluti water and surrounding groundwater varied markedly with seasons, depth and locations. Range, mean and standard deviation values for physicochemical parameters from L. Duluti and surrounding groundwater sources are presented in Table 1 below.

Table 1a: Descriptive statistics of physico-chemical parameters of water from Lake Duluti

Parameters	Dry Season			Wet Season		
	Max	Min	Mean	Max	Min	Mean
pH	8.93	8	8.6±0.3	9.8	8.7	9.3±0.3
EC (µS/cm)	570	524	547.6±14.1	646	510	530±31.0
TDS (ppm)	285	262	273.4±6.6	323	255	264.3±15.6
Temp (°C)	27.7	24.6	25.8±1.0	27.8	25	25.8±0.9
Na (mg/l)	42.4	41	41.7±0.3	42.4	34.8	39.5±2.3
K (mg/l)	8	5.2	6.3±0.9	8.3	4.3	6.1±1.2
Ca (mg/l)	18	16.4	17.1±0.4	19.2	12	16.8±1.9
Mg (mg/l)	7.7	6.3	7.0±0.4	8.5	2.4	5.9±1.8
Cl (mg/l)	14.5	8.5	10.6±1.7	10.5	7.5	8.7±0.7
SO$_4$ (mg/l)	5	1	1.7±1.0	8	0	2.4±2.2
NO$_3$ (mg/l)	2	0.8	1.2±0.4	2.4	1.2	1.6±0.3
HCO$_3$ (mg/l)	167.2	134.7	150.5±10.0	155.4	81.6	117.0±20.1
CO$_3$ (mg/l)	11.3	1.4	6.9±3.1	34.8	7.3	21.3±8.1
F (mg/l)	3.3	3	3.1±0.1	2.6	2.3	2.5±0.1

Table 2b: Descriptive statistics of physico-chemical parameters of water from Springs

Parameters	Dry Season			Wet Season		
	Max	Min	Mean	Max	Min	Mean
pH	7	6.5	6.8±0.3	7.6	7	7.3±0.2
EC (µS/cm)	549	377	436.7±97.3	565	196	360.8±139.3
TDS (ppm)	274	189	218.3±48.2	282	98	180.2±69.5
Na (mg/l)	19	10	14.0±4.6	18.3	5.2	11.8±4.7
K (mg/l)	4.1	1.6	3.0±1.3	4.3	1.7	3.0±1.2
Ca (mg/l)	32.1	24	27.8±4.1	31.6	15.5	23.6±6.1
Mg (mg/l)	7.9	4.8	6.5±1.6	7.3	3.4	5.0±1.8
Cl (mg/l)	13.5	2.5	8.8±5.7	16	0.5	6.6±6.7
SO$_4$ (mg/l)	9	6	7.3±1.5	14	4	9.2±3.9
NO$_3$ (mg/l)	1.6	0.6	1.2±0.5	4.4	1.6	2.8±1.2
HCO$_3$ (mg/l)	121.2	87.3	102.4±17.3	120.8	64	94.5±20.6
CO3 (mg/l)	0.1	0	0.1±0.0	0.4	0.1	0.2±0.2
F (mg/l)	1.6	1.5	1.5±0.1	1.2	0.4	0.9±0.3

Table 3c: Descriptive statistics of physico-chemical parameters of water from Boreholes

Parameters	Dry Season			Wet Season		
	Max	Min	Mean	Max	Min	Mean
pH	8.5	6.8	7.2±0.5	8.5	7.1	7.7±0.5
EC (µS/cm)	885	337	549.2±201.8	888	376	563.9±187.1
TDS (ppm)	442	169	274.8±100.8	444	188	282.3±93.4
Na (mg/l)	28.1	16.2	19.2±3.6	18	15.4	16.9±0.9
K (mg/l)	5.8	1.5	3.1±1.2	6.1	1.7	3.2±1.3
Ca (mg/l)	24.2	19.1	22.4±1.5	23.7	18.3	21.8±1.5
Mg (mg/l)	10.4	6	7.3±1.4	9.8	5.2	6.6±1.4
Cl (mg/l)	16.5	2	8.7±5.0	16	2	8.7±4.8
SO$_4$ (mg/l)	9	0	5.2±3.6	10	6	7.9±1.3
NO$_3$ (mg/l)	6.1	0.4	2.8±1.6	4.2	1.3	3.2±0.8
HCO$_3$ (mg/l)	252.6	84.5	140.5±64.3	130.2	97.8	106.0±10.1
CO$_3$ (mg/l)	6.7	0.1	0.9±2.2	2.9	0.2	0.9±1.0
F (mg/l)	4.1	1.3	2.2±1.2	4	0.8	1.7±1.2

Generally, pH of L. Duluti water was alkaline for both seasons while that of surrounding groundwater sources was slightly acidic to slight alkaline during the dry season and neutral to slightly alkaline during the wet season. The mean pH of the Lake was 8.6±0.3 during the dry season and 9.3±0.3 during the wet season (Table 1a). On the other hand, mean pH of the springs was 6.79±0.25 and 7.2±0.22 while that of boreholes was 7.21±0.5 and 7.72±0.5 during dry and wet seasons, respectively (Table 1b and 1c). The pH of the Lake water was significantly higher ($p<0.01$) than that of the groundwater during the two seasons. Furthermore, the pH of all sampled water sources was significantly higher ($p<0.01$) during wet season than respective water samples during the dry season. The pH of the lake water during dry season was stable on the top two meters and then showed a sharp decreasing trend with increasing depth from below two meters (Fig 4a, b). In contrast it showed a general decrease with depth during rainy season (Fig. 4b).

The water temperature, which was relatively high in the lake than in surrounding groundwater sources showed no significant difference ($p<0.05$) between seasons. In the Lake water, temperature had a mean of 25.8±1.0 °C during the dry season and 25.8±0.9 °C during the wet season. Mean temperature for groundwater were 23.1±2.5 and 23.0±2.7 °C during the dry and wet wet seasons, respectively.

Furthermore, the dissolved oxygen (DO) in the lake had a mean of 3.1±0.4 mg/l and 4.0±0.5 mg/l, and boreholes 2.1±0.8 mg/l and 2.7±0.5 mg/l during dry and wet seasons, respectively. Means for springs were 2.9±0.4 mg/l during the dry season and 4.2±0.6 mg/l during the wet season. Higher EC values were observed in boreholes for both seasons relative to the Lake and springs. In the Lake, EC had a mean of 547±14.1 and 530±31 (µS/cm) during dry and wet seasons, respectively and increased with depth.

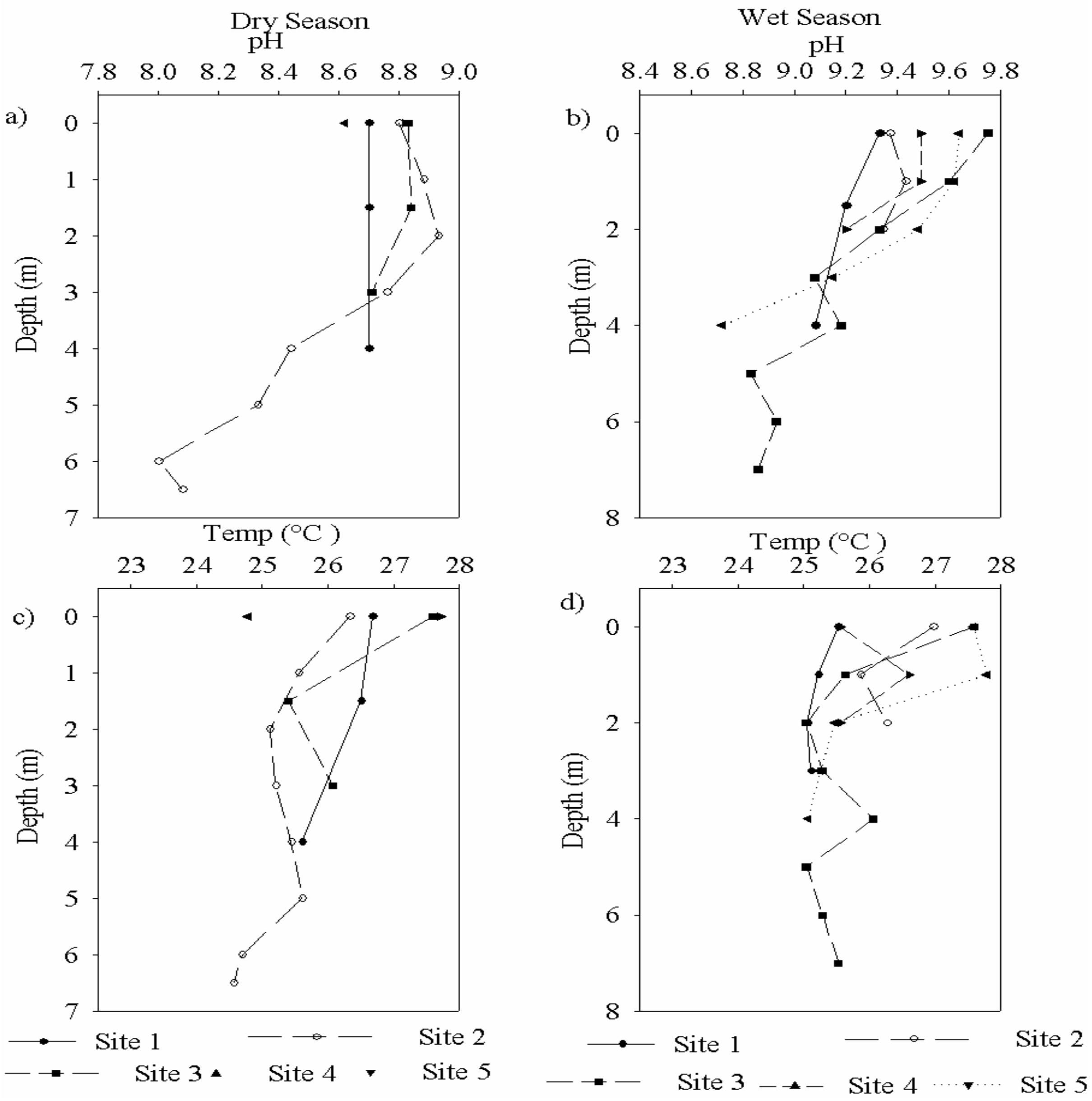


Figure 4: Seasonal variations (dry and wet seasons) in pH (a, b) and Temperature (c, d) with depth

The EC mean for boreholes during dry and wet seasons were 549±201.76 and 563.9±187.1 while in springs respective values for EC were 436.±97.3 and 360±139.2 (Table 1b and 1c; Fig. 5) during dry and wet seasons. The mean TDS values were 273.4±6.6 and 264.3±15.6 mg/l in the Lake, 218.3±48.2 and 180.2±69.5 mg/l in springs and 274.8±100.8 and 282.3±93.4 mg/l in boreholes during dry and wet seasons.

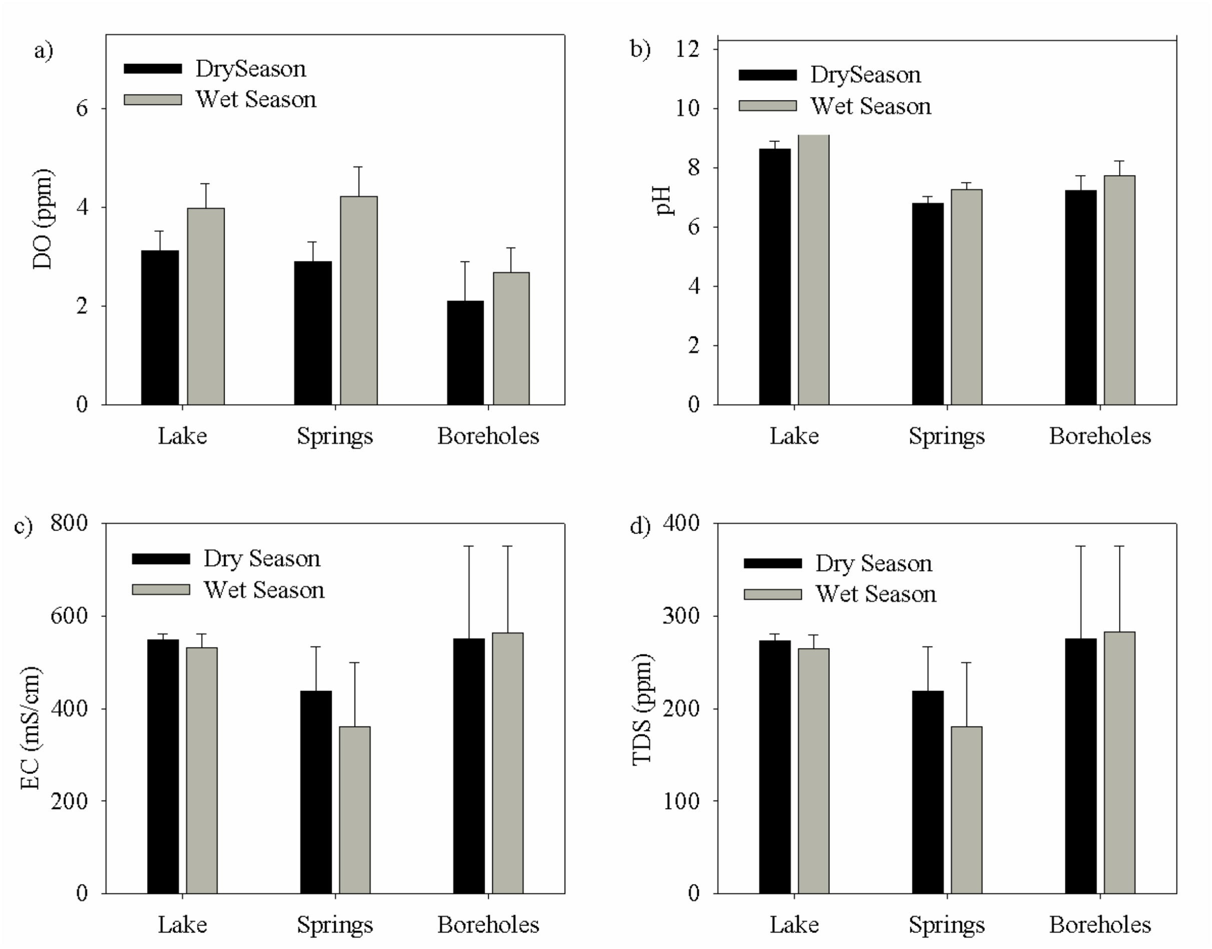


Figure 5: Mean values respective standard deviations for physico-chemical parameters (a) DO (mg/l), (b) pH, (c) EC (µS/cm) and (d) TDS

3.3.2 Chemical characteristics of major ions

(i) Sodium

Concentration of Sodium ion in the lake water averaged 41.7±0.3 and 39.5±2.3 during the dry and wet seasons, respectively (Table 1a). Similarly, average concentrations of Sodium ion in the springs were 14±4.5 and 11.8±4.7 during dry and wet seasons while respective values for boreholes were 19.1±3.6 and 16.8±0.91 (Fig. 6). The concentration of Na^+ was significantly higher ($p<0.01$) in Lake water than in surrounding groundwater (springs and boreholes) (Fig. 6) and tend to increase with depth during wet season (Fig. 6). Sodium concentration decrease with depth during dry season and slightly varied with depth during wet season (Fig. 6).

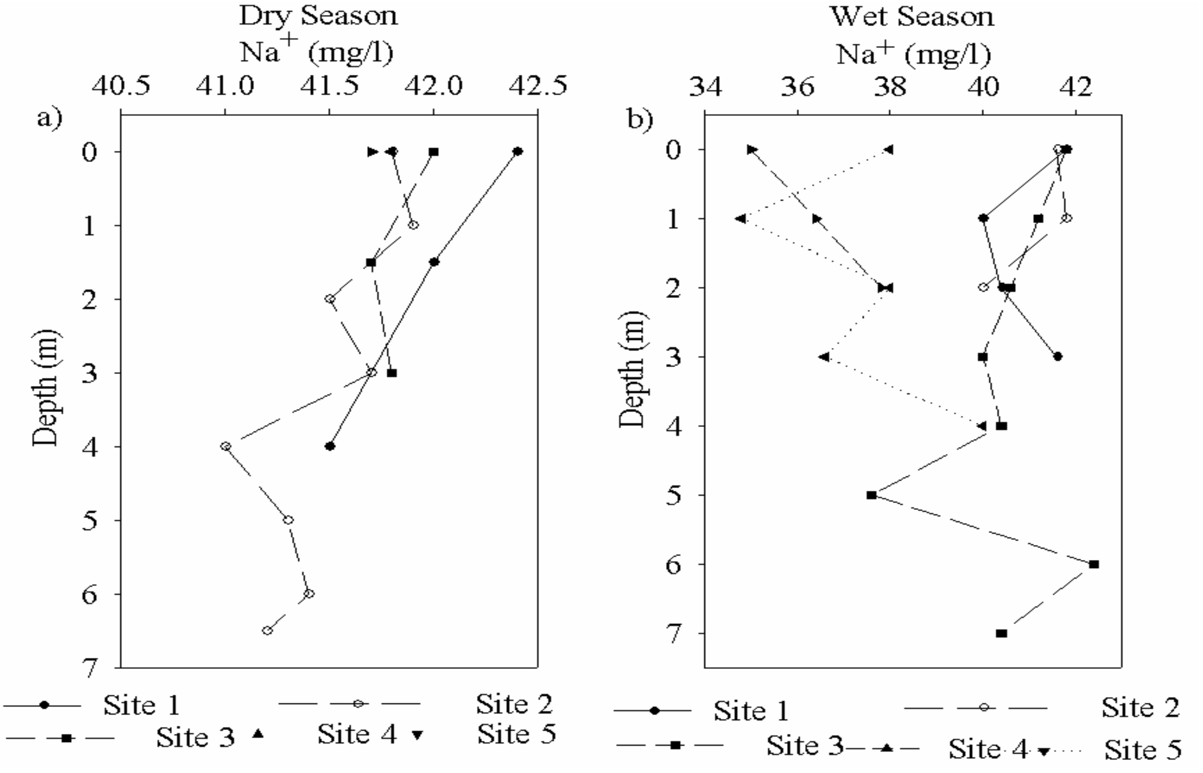


Figure 6: Variation of Sodium with depth during (a) dry and (b) wet season

(ii) Calcium

In the lake water, mean calcium ion concentration was 17.1±0.4 and 16.8±1.9 mg/l during dry and wet seasons, respectively (Table 1a; Fig. 7) and the concentration slightly varied with depth during dry season and wet season. Concentration of Calcium in springs averaged 27.8±4.07 and 23.6±6.09 during dry and wet seasons and values of boreholes were 22.4±1.4 and 21.7±1.5, respectively (Table 1b; Fig. 7). Concentration of Ca^{2+} was significantly higher ($p<0.01$) in the springs and boreholes than in the lake (Fig. 7).

(iii) Magnesium

Mean concentrations of Magnesium ion in the Lake water were 7.0±0.4 and 5.9±1.8 mg/l during dry and wet seasons, respectively. Corresponding values for springs were 5.9±1.8 mg/l during dry and 5.9±1.8 wet seasons while those of boreholes were 7.3±1.3 and 6.6+1.4, respectively. There was no significant variation in Mg^{2+} with water sources in both seasons ($P >0.05$).

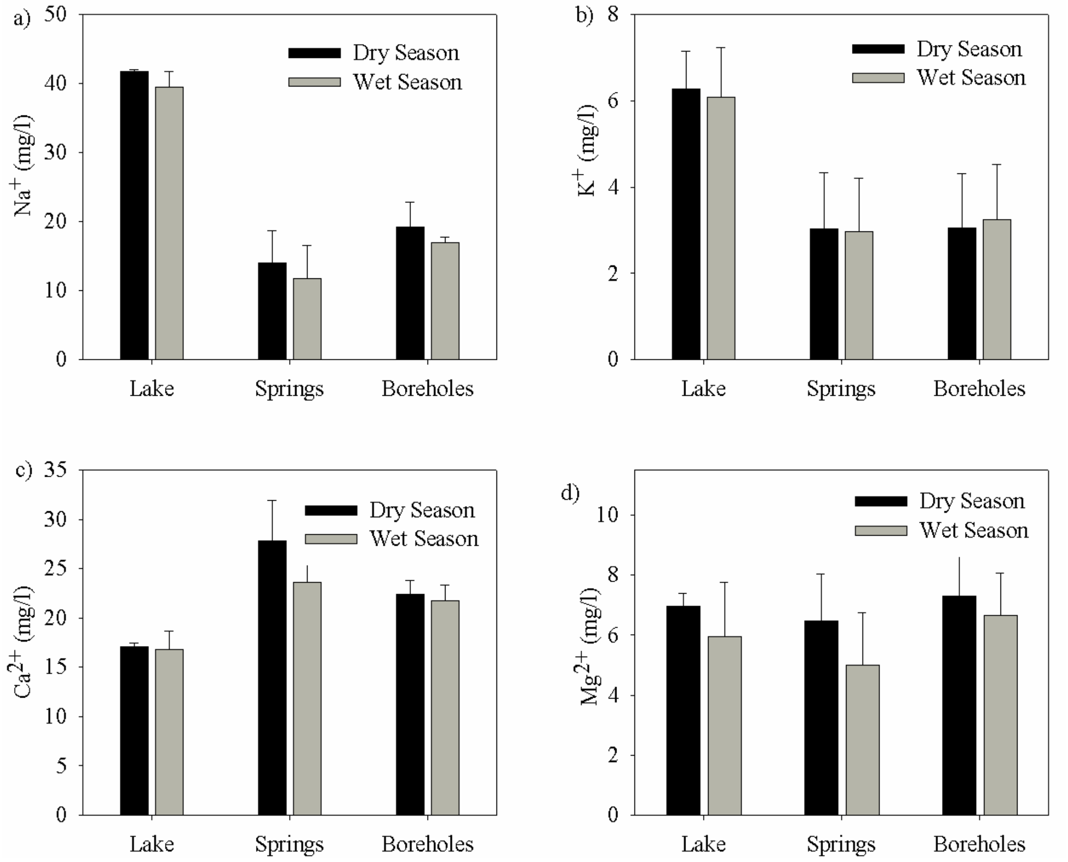


Figure 7: Seasonal variability in concentration of chemical parameters (a) Na$^+$ (mg/l), (b)K$^+$ (mg/l) (c) Ca^{2+} (mg/l) and (d) Mg^{2+} (mg/l) for various water sources

(iv) Potassium

Mean Potassium concentrations in lake water were 6.3±0.9 mg/l and 6±1.3mg/l during the dry and wet seasons (Table 1a; Fig. 7), respectively, while in springs corresponding values were 3.03±1.2 mg/l and 2.9±1.2 mg/l, and for boreholes 3.05±1.2 and 3.2±1.2, respectively. Concentration of K$^+$ in the lake water was significantly higher ($p<0.01$) than in the surrounding groundwater sources (Fig. 7b), and decreased with depth during dry and wet season.

3.3.3 Chemical characteristics of anions

(i) Fluoride

In the lake, the mean concentrations of F$^-$ were 3.1±0.1 mg/l and 2.5±0.1 mg/l during dry and wet seasons, respectively. Similarly, the respective concentrations of F$^-$ in springs were 1.5±0.05 and 0.9±0.2 whilst those of boreholes were 2.2±1.16 and 1.74±1.1 respectively (Table 1a, 1b and 1c; Fig. 8). The F$^-$ concentration in lake water was significantly higher ($p<0.01$) than in boreholes and springs during the two seasons (Fig. 9).

(ii) Chloride

The concentrations of Cl^- in the lake water were 10.6±1.7 mg/l and 8.7±0.7 mg/l during dry and wet seasons while in springs respective values were 8.8±5.6 and 6.5±6.6 mg/l. The concentration of chloride in boreholes averaged 8.6±4.9 during dry season and averaged 8.6±4.8 mg/l during wet seasons, as in (Table 1c; Fig. 8). The concentration of Cl^- was slightly higher in lake water than groundwater during the two seasons although the difference was not significant. Also there was no significant variation of Cl^- concentration with seasons (Fig. 8).

(iii) Sulfate

The mean concentrations of SO_4^{2-} in Lake Duluti were 1.7±1.0 and 2.4±2.2 mg/l during dry and wet seasons, respectively. Respective values for springs were 7.3±1.5 and 9.2±3.8 mg/l and those for boreholes were 5.2±3.6 and 7.8±1.3 mg/l (Fig. 8). The concentration of SO_4^{2-} in Lake Duluti water was significantly lower ($p<0.01$) than in the surrounding groundwater. During the wet season, the concentration of SO_4^{2-} in groundwater. was higher than dry season, and concentration in the lake water was observed to be significantly higher ($p<0.05$) in wet season than during the dry season.

(iv) Bicarbonate and Carbonate

Mean concentrations of HCO_3^- in the lake water were 150.5±10.0 and 117.0±20.1 mg/l during dry and wet seasons, for springs 102.4±17.3 131±58 and 94.5±20.6 mg/l while boreholes had mean concentrations of 140.5±64.3 mg/l and 106.0±10.1 mg/l during dry and wet seasons, respectively.

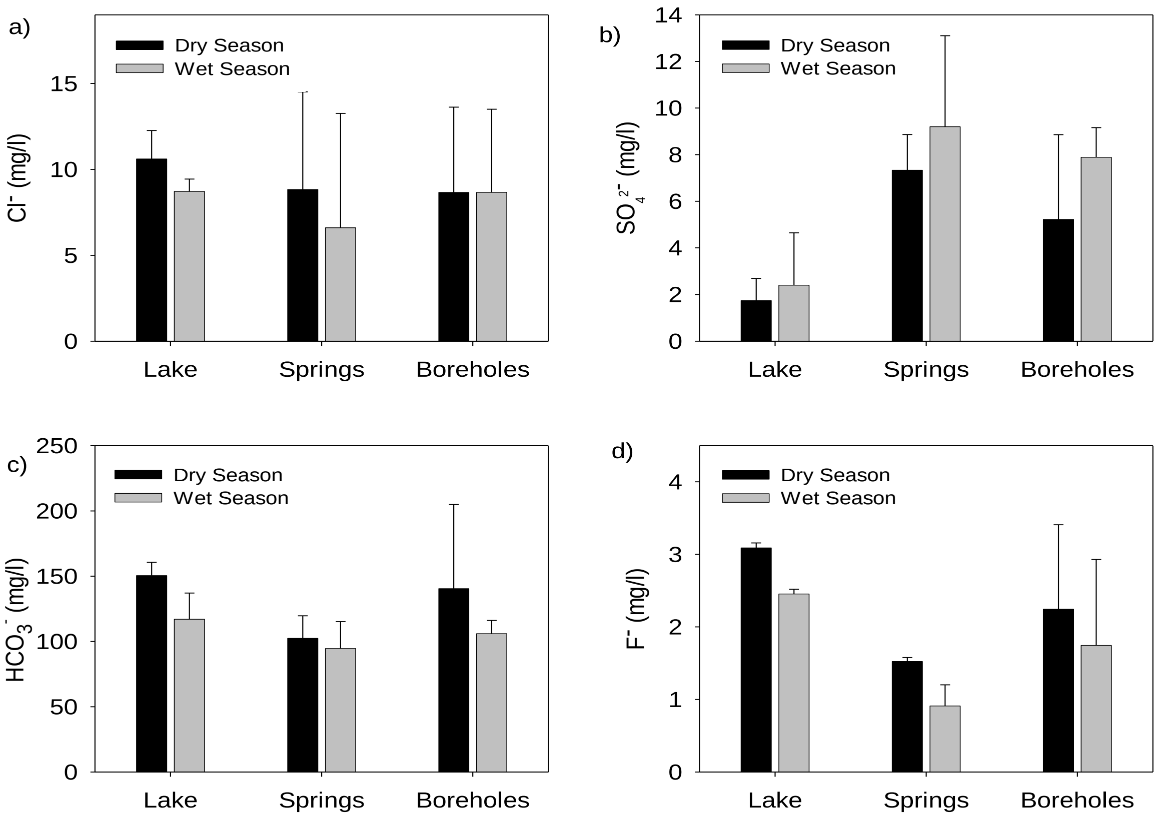


Figure 8: Seasonal variability in concentration of chemical parameters (a) Cl^- (mg/l), (b) SO_4^{2-}(mg/l) (c) HCO_3^- (mg/l) and (d F^- (mg/l) for various water sources

The concentration of HCO_3^- was significantly higher in lake water ($p<0.01$) and was also observed to be higher during the dry season than during the wet seasons in groundwater sources. Furthermore, there was a general increase in concentration of HCO_3^- in the lake water with respect to depth, which was significant ($p<0.01$) during the wet seasonal.

The concentration of CO_3^{2-} for the lake water averaged 6.9±3.1 mg/l during dry season and 21.3±8.1 mg/l during wet season, whereas mean values for boreholes water were 0.9±1.0 and 0.9±0.0 mg/l during dry and wet seasons, respectively. The concentration of CO_3^{2-} in spring waters were 0.1±0.0 and 0.2±0.2 in during dry and wet seasons, respectively. The concentration of CO_3^{2-} was significantly higher ($p<0.01$) in lake water than in surrounding groundwater sources during the two seasons. Additionally, the concentration of CO_3^{2-} in lake water was significantly higher during wet season than during dry season. The concentration of CO_3^{2-} showed a decreasing trend with lake water depth (Fig. 9).

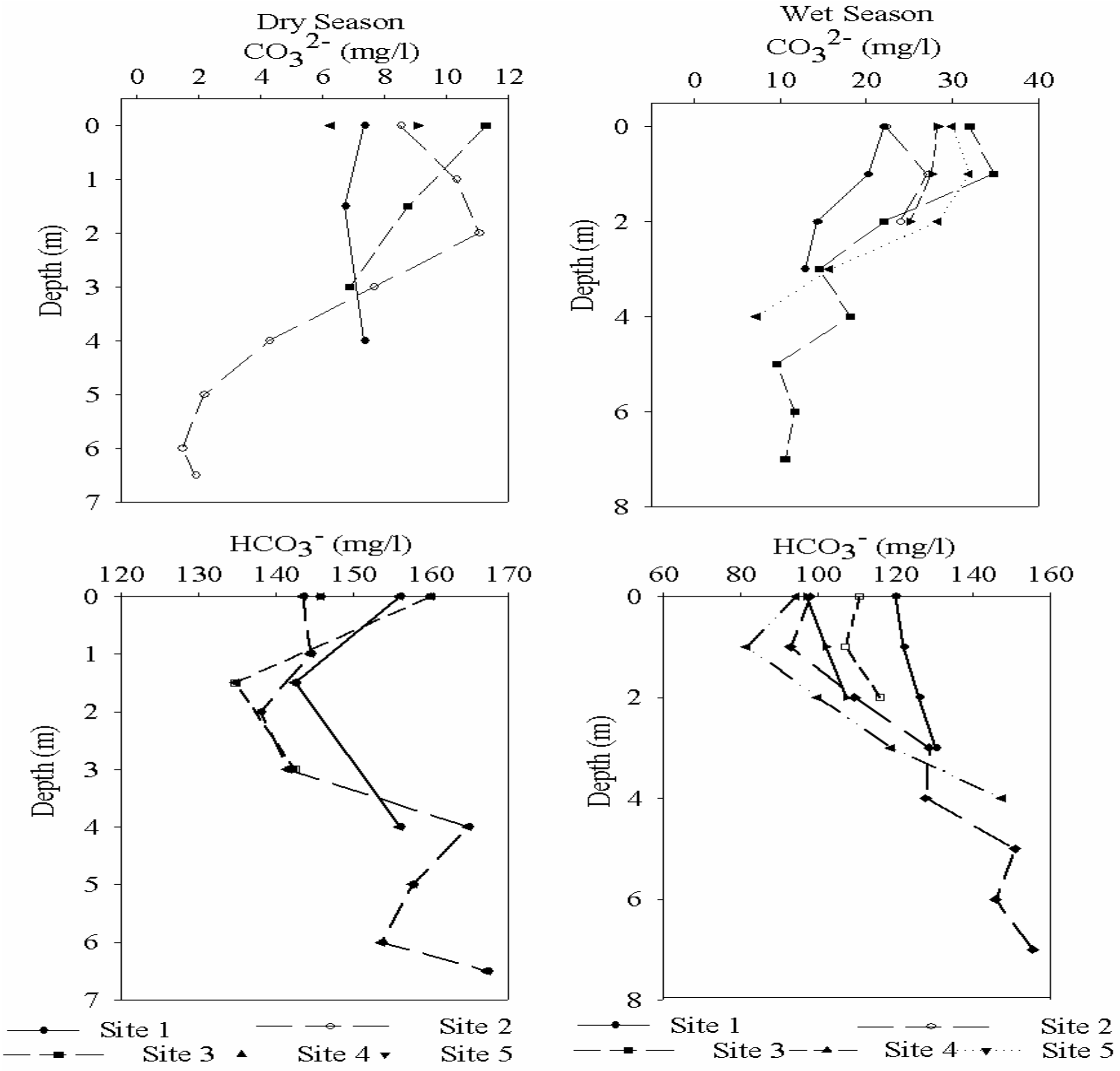


Figure 9: Variation of Bicarbonate (a) during dry season, (b) during wet season and Carbonate (c) during dry season, (d) during wet season with depth

(i) *Nitrate*

The concentrations of NO_3^- in the lake water were 1.2±0.4 and 1.6±0.3 mg/l during dry and wet seasons while in springs respective values were 1.2±0.5 mg/l and 2.8±1.2 mg/l. Similarly, values for boreholes were 2.8±1.6 and 3.2±0.8 mg/l, respectively. The concentration of NO_3^- was significantly lower ($p<0.01$) in lake water than in surrounding groundwater sources.

Plate 1: Part of L. Duluti overgrown with macrophytes (sedges and papyrus)

3.3.4 Interrelation of chemical parameters

Correlation Matrix was used to evaluate the interrelationships among physico-chemical parameters of L. Duluti water and surrounding groundwater sources. Correlations among physico-chemical parameters in L. Duluti water are presented in Tables 2 and 3 while for surrounding groundwater are presented in Tables 4 and 5. The pH showed significant negative correlation with EC, TDS, HCO_3^- (r=-0.69,-0.76,-0.63, $p \leq 0.05$), and significantly positive correlation with temperature, CO_3^{2-} ($p \leq 0.01$, r = 0.51, 0.94; respectively) during dry and wet seasons. Also, pH showed significant positive correlation with $Na^+$and Ca^{2+} (r=0.58, 0.61, $p \leq 0.05$) during the dry season. The EC and TDS showed significant positive correlation with temperature, HCO_3^- at ($p \leq 0.05$, r=0.55, 0.57), and negative correlation with CO_3^{2-} at ($p \leq 0.05$, r=-0.65, -0.72) during dry and wet season. In the Lake water Na^+ showed significant positive relationship with K^+ ($p \leq 0.01$, r=0.65), Ca^{2+}, Cl^-, CO_3^{2-} at ($p \leq 0.05$, r=0.53, 0.60, 0.58) and negative correlation with F^- during dry and wet seasons. It was also observed that K^+ to have significant positive correlation with Ca^{2+} ($p \leq 0.05$, r=0.51), Mg^{2+} ($p \leq 0.01$, r=0.67).

Table 4: Correlaions coefficient (r) between physic-chemical paameters for Lake Duluti during Dry Season

	Depth	DO	pH	EC	TDS	Temp	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	HCO_3^-	CO_3^{2-}	F^-
Depth	1															
DO	-0.68**	1														
pH	-0.81**	0.47	1													
EC	0.64**	-0.39	-0.69**	1												
TDS	0.68**	-0.43	-0.76**	0.98**	1											
Temp	-0.64**	0.66**	0.50*	-0.26	-0.29	1										
Na^+	-0.77**	0.52*	0.58*	-0.33	-0.37	0.55*	1									
K^+	-0.55*	0.11	0.40	0.02	-0.04	0.38	0.64**	1								
Ca^{2+}	-0.56*	0.51*	0.60*	-0.31	-0.38	0.57*	0.53*	0.50*	1							
Mg^{2+}	-0.27	-0.18	0.42	-0.02	-0.07	0.20	0.37	0.67**	0.32	1						
Cl^-	-0.34	0.08	0.30	-0.13	-0.12	0.23	0.60*	0.34	0.05	0.23	1					
SO_4^{2-}	-0.28	0.50*	0.02	-0.19	-0.20	-0.13	0.07	0.01	0.09	-0.18	-0.12	1				
NO_3^-	-0.29	0.52*	0.12	-0.17	-0.19	0.19	0.10	0.02	0.32	0.03	-0.13	0.78**	1			
HCO_3^-	0.37	-0.05	-0.63**	0.55*	0.56*	-0.12	-0.35	-0.07	-0.45	-0.37	-0.19	0.27	0.17	1		
CO_3^{2-}	-0.79**	0.45	0.94**	-0.65**	-0.72**	0.51*	0.57*	0.35	0.46	0.48	0.26	0.02	0.20	-0.55*	1	
F^-	0.19	-0.29	-0.26	-0.01	0.04	-0.46	-0.51*	-0.37	-0.29	-0.25	-0.43	0.33	0.33	0.25	-0.18	1

*Significant at $p \leq 0.05$; **Significant at $p \leq 0.01$

Table 5: Correlations coefficient (r) between physico-chemical parameters for Lake Duluti during wet seasons

	Depth	DO	pH	EC	TDS	Temp	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	HCO_3^-	CO_3^{2-}	F^-
Depth	1															
DO	-0.80**	1														
pH	-0.82**	0.69**	1													
EC	0.25	0.11	-0.41*	1												
TDS	0.29	0.04	-0.43*	0.98**	1											
Temp	-0.50*	0.49*	0.71**	-0.25	-0.31	1										
Na^+	0.15	0.19	-0.21	0.36	0.33	-0.20	1									
K^+	-0.27	0.32	0.06	0.26	0.29	-0.01	-0.12	1								
Ca^{2+}	0.33	-0.55**	-0.40	0.04	0.05	-0.45*	-0.23	-0.08	1							
Mg^{2+}	0.05	-0.09	-0.12	0.10	0.07	-0.43*	0.10	-0.01	0.60**	1						
Cl^-	0.34	-0.33	-0.07	-0.15	-0.17	0.08	-0.09	-0.32	0.05	0.13	1					
SO_4^{2-}	0.01	0.08	-0.10	-0.18	-0.15	-0.21	0.32	0.13	-0.21	0.10	-0.32	1				
NO_3^-	-0.08	0.32	0.14	0.02	0.04	-0.01	0.32	-0.06	-0.20	0.19	-0.20	0.48*	1			
HCO_3^-	0.83**	-0.59**	-0.9**	0.50*	0.52**	-0.6**	0.37	-0.05	0.28	0.10	0.10	0.12	-0.15	1		
CO_3^{2-}	-0.78**	0.62**	0.96**	-0.42*	-0.43*	0.64**	-0.25	0.03	-0.29	-0.05	-0.08	-0.12	0.16	-0.9**	1	
F^-	0.21	-0.28	-0.25	0.29	0.32	-0.06	-0.42*	0.31	0.31	-0.09	-0.04	-0.31	-0.16	0.1868	-0.24	1

*Significant at $p \leq 0.05$; **Significant at $p \leq 0.01$

Table 6: Correlations coefficient (r) between physico-chemical parameters for Groundwater sources during Dry season

	Depth	DO ppm	pH	EC	TDS	Temp	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	HCO_3^-	CO_3^{2-}	F^-
Depth	1															
DO	-0.59*	1														
pH	0.15	0.34	1													
EC	-0.08	0.29	0.61*	1												
TDS	-0.08	0.29	0.61*	1**	1											
Temp	0.10	0.18	0.67*	0.87**	0.87**	1										
Na^+	0.75**	-0.56	-0.10	0.10	0.10	0.13	1									
K^+	-0.10	-0.13	-0.16	-0.06	-0.06	-0.16	-0.08	1								
Ca^{2+}	-0.7**	0.47	-0.29	-0.02	-0.02	-0.13	-0.41	0.34	1							
Mg^{2+}	0.06	0.28	0.74**	0.64*	0.64*	0.68*	0.11	0.19	0.18	1						
Cl^-	-0.11	0.08	0.33	0.56	0.56	0.49	-0.01	0.12	0.31	0.59*	1					
SO_4^{2-}	-0.47	0.88**	0.41	0.16	0.16	0.15	-0.6*	-0.16	0.40	0.32	0.06	1				
NO_3^-	0.51	-0.58*	0.17	0.12	0.11	0.22	0.32	-0.15	-0.36	0.18	0.58*	-0.40	1			
HCO_3^-	0.11	0.13	0.68*	0.85**	0.85**	0.97**	0.21	-0.24	-0.15	0.69*	0.43	0.11	0.19	1		
CO_3^{2-}	0.05	0.28	0.89**	0.65*	0.64*	0.69*	-0.05	-0.10	-0.12	0.76**	0.50	0.23	0.20	0.69*	1	
F^-	0.08	0.16	0.81**	0.45	0.44	0.51	-0.10	0.01	-0.04	0.80**	0.38	0.41	0.24	0.57	0.66*	1

* Significant at p $p \leq 0.05$; **Significant at $p \leq 0.01$

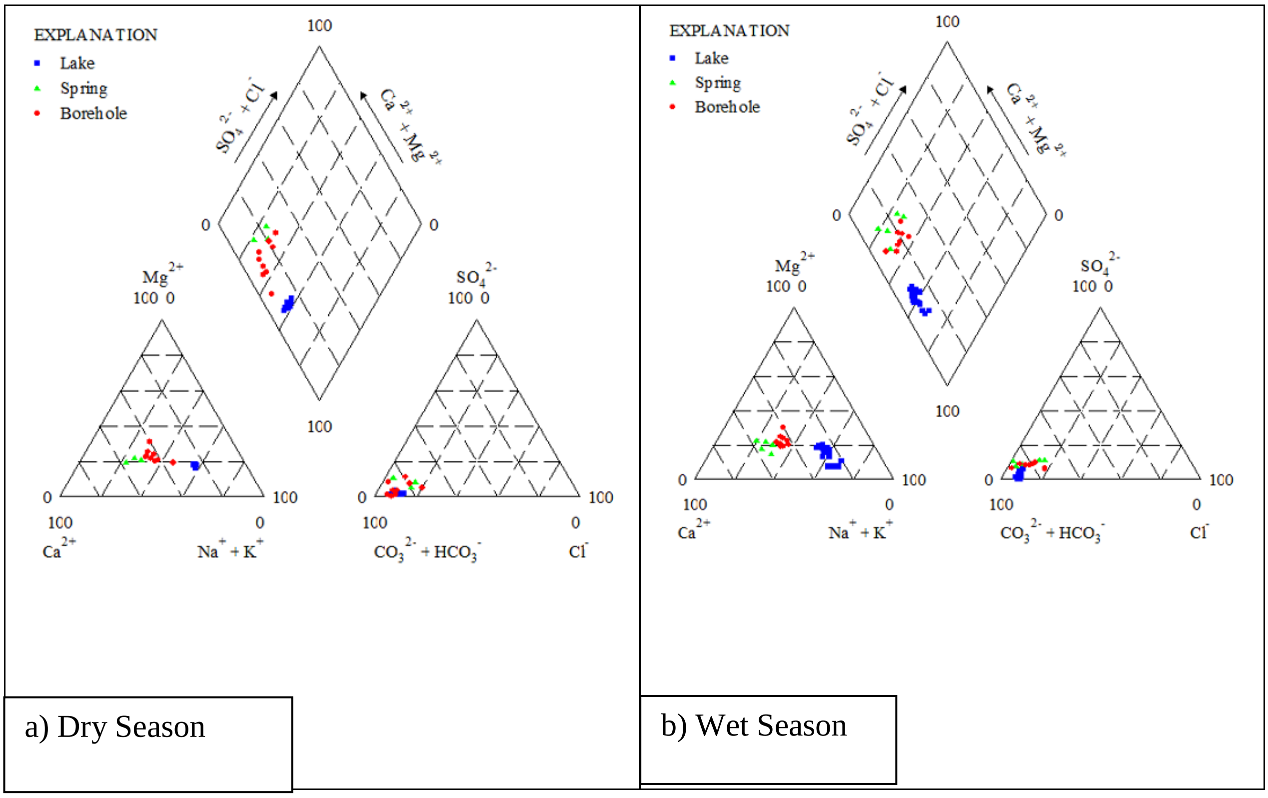
Table 7: Correlations coefficient (r) between physico-chemical parameters for Groundwater sources during Wet season

	Depth	DO	pH	EC	TDS	Temp	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	NO_3^-	HCO_3^-	CO_3^{2-}	F^-
Depth	1															
DO	-0.42	1														
pH	0.19	-0.49	1													
EC	0.29	-0.71**	0.55*	1												
TDS	0.30	-0.71**	0.55*	0.99**	1											
Temp	0.39	-0.79**	0.64*	0.89**	0.89**	1										
Na^+	0.57*	-0.69**	0.43	0.69**	0.69**	0.62*	1									
K^+	0.01	-0.01	0.18	0.08	0.09	0.04	0.45	1								
Ca^{2+}	-0.34	-0.37	0.26	0.26	0.26	0.18	0.42	0.49	1							
Mg^{2+}	0.31	-0.74**	0.78**	0.80**	0.80**	0.87**	0.65*	0.28	0.44	1						
Cl^-	0.13	-0.31	0.31	0.59*	0.60*	0.491	0.56*	0.58*	0.56*	0.65*	1					
SO_4^{2-}	-0.19	-0.39	0.07	0.23	0.23	0.16	0.38	0.21	0.86**	0.32	0.43	1				
NO_3^-	0.28	-0.34	0.17	0.46	0.46	0.41	0.51	0.27	0.42	0.47	0.83**	0.52	1			
HCO_3^-	0.19	-0.69**	0.51	0.52	0.52	0.55*	0.79**	0.57*	0.68**	0.68**	0.43	0.47	0.22	1		
CO_3^{2-}	0.17	-0.40	0.89**	0.49	0.49	0.64*	0.28	0.08	0.13	0.77**	0.22	-0.12	-0.01	0.45	1	
F^-	0.16	-0.56*	0.79**	0.64*	0.64*	0.78**	0.34	0.05	0.12	0.78**	0.21	-0.08	-0.09	0.51	0.90**	1

*Significant at $p \leq 0.05$; **Significant at $p \leq 0.01$

3.3.5 Hydro-geochemical facies

The Hydro-chemical water type of water samples from L. Duluti and surrounding groundwater sources in dry and wet seasons from the study area is represented in Piper diagram below where concentration is assigned in % meq/L.



a) Dry Season

b) Wet Season

Figure 10: Piper trilinear diagram for Facies Classification in dry season and wet season

The hydrochemistry of the sampled water shows that there is a clear distinction between the lake, spring, river, and boreholes samples collected in the studied area. This is clearly shown in a Piper diagram above (Fig. 10) by plotting the major ions of water chemistry on a single four sided diagram. The Piper diagram describes the composition of water and classifies it into ionic type based on the dominant cation and anions. Plot of lake water results on the diamond diagrams were observed to fall within the alkali metals than alkali earth metals ($Na^+ + K^+ > Ca^{2+} + Mg^{2+}$). Weak acid anions were dominant over strong acid anions ($HCO_3^- > SO_4^{2-} + Cl^-$). Therefore, based on this classification, the water types found in the study area with respect to the water sources are Na-HCO_3 type for L. Duluti, Ca-HCO_3 and Ca-Na-HCO_3 types for springs and boreholes, respectively.

3.4 Discussion

In the study conducted to assess the physic-chemical characteristics of Lake Duluti and its relation to groundwater sources, pH of the Lake, which was found to be mildly alkaline ($pH>7$) may have been a result of natural processes including contribution by surrounding alkaline rocks (Wilkinson *et al.*, 1986; Öberg *et al.*, 2012). Similar observation was reported by Öberg *et al.* (2012). The observed decreasing trend of pH was probably due to decomposition of organic matter and respiration occurring in the lower water levels. Slightly acidic to slightly alkaline values were recorded for groundwater sources (springs and boreholes) in Meru district, which have also been reported by Elisante and Muzuka (2015).

Water temperature fluctuations occurred between different points of the Lake water column due to response to incomplete mixing or homogenization by wind leading to stratification (Fig. 5c and Fig. 5d). Thermal stratification in Lake Duluti occurs at a depth of 2 m from the surface where the top 2 m are well mixed and aerated while poor mixing occurs at the depth below 2 m. Similar observation was observed in this study where the top 2 m of lake water showed higher temperature than the lower levels (Öberg *et al.*, 2012). Due to low temperatures recorded in the bottom water, such water was denser than the top water a likely cause of poor mixing of the lake water. Poor mixing affected the distribution of DO and pH within the Lake. Lower temperatures at the bottom of the lake could also be an indication of groundwater input or flux to the lake. This is supported by the results of oxygen isotopes which showed a general decreasing trend in isotopic composition with depth (Fig. 14).

It was observed that DO decreased significantly with increasing depth during the dry season ($r=-0.68$, $p<0.01$) and ($r=-0.80, p<0.01$) in wet season probably due to the fact that, wind overturning is not enough to cover the water column. The EC and TDS values in the lake water and groundwater, which showed no significant differences, were likely to be a result of inlet and outlet of lake water through groundwater.

Sodium, which was the dominant cation in the lake water was likely to be a result of silicate weathering and/or dissolution of soil salts discharged into lake water through groundwater (Subbarao *et al.*, 1996; Mamatha & Rao, 2010; Rao *et al.*, 2012). However, it has been observed that the rate of accumulation of some ions like Na^+ in the lake water is very low due to loss of ions to groundwater, this has also been reported earlier that L. Duluti looses some ions through the groundwater (Öberg *et al.*, 2012). Furthermore, ion exchange influences the higher contribution of Na^+ than that contributed by Ca^{2+}. The concentration of Ca^{2+} in the lake water, which was significantly lower than in the surrounding springs and boreholes was likely to be a result of precipitation as $CaCO_3$ due to high concentration of $HCO^{3-}$and CO_3^{2-} in the lake water (Anazawa, 2001). Lake Duluti was observed to have a higher concentration of K^+ as compared to the groundwater sources probably due to cumulative effect as water comes from the ground.

The observed higher concentration of fluoride in lake water than the surrounding groundwater was probably a result of accumulation due to evapo-transpiration. It is very likely that, the lake receives water from the ground with low concentration of F^-, which later accumulates as the water evaporates. In addition, the dominance of Na^+ and HCO_3^- ions in the lake indicates precipitation of Ca^{2+} as $CaCO_{3.}$ Few groundwater sources around the Lake had relatively high fluoride concentration a likely result of interaction of water with the volcanic rocks rich in F- and alkali (Ghiglieri *et al*., 2010).

The concentration of Cl^- was relatively high in the Lake water than groundwater during the two seasons although the difference was not significant. Also, there was no significant variation of Cl^- concentration with seasons. Probably, the main sources of Cl^- in the Lake and surrounding groundwater sources is dissolution of salt deposits and weathering The observed significantly high concentration of carbonate in the lake water than in surrounding springs and boreholes was likely as a function of dissolved carbon dioxide, temperature, pH, cations and other dissolved salts.

Groundwater sources were observed to have higher concentration of SO_4^{2-} than the concentration observed in the lake. This may be contributed to dissolution of salts deposits and contamination caused by different human activities such as agricultural activities and livestock keeping. The concentration of NO_3^- in lake water was significantly lower ($p<0.01$) in lake water than in surrounding groundwater. This could be attributed to either minimum anthropogenic input or high primary productivity of macrophytes and phytoplankton. During fieldwork, it was noted that shallow lake areas have been colonized by macrophytes vegetation such as papaylus (Plate 1). Such plants have been used in constructed wetland to reduce nutrient loading in waste water (Gottschall, 2007). Elevated nitrate concentration (above 10 mg/L) was observed in some of the surrounding groundwater sources indicating pollution due to agriculture and sanitation facilities. Similar elevated nitrate concentration due to contamination with sewage and animal manure in groundwater source in Meru district have been reported by Elisante and Muzuka (2015).

Negative correlation of pH with EC, TDS, HCO_3^- was observed among physico-chemical parameters in L. Duluti and also had significantly positive correlation with temperature during both seasons. Significant positive correlation of pH with $Na^+$and Ca^{2+} during the dry season was also observed, this shows that, the Lake water is characterized by alkaline surroundings, which tends to dissolve aquifer minerals such as fluoride-bearing minerals. Significant positive correlation of EC and TDS with temperature, HCO_3^- and negative correlation with CO_3^{2-} during dry and wet season indicates that, the Lake is mainly controlled by HCO_3^- ions, which depend upon respiration of aquatic organisms, decomposition of organic matter and mineral solubility. Significant positive relationship of Na^+ with K^+, Ca^{2+}, Cl^-, CO_3^{2-} and negative correlation with F^- on both seasons, indicates the influence of evaporation and dissolution of minerals. Significant positive correlation of K^+ with Ca^{2+} indicates mineral dissolution and SO_4^{2-} showed positive correlation with NO_3^- at 95% confidence level indicating oxidation of organic matter.

The results also shows there is local system of ground-water flow, as recharge and discharge areas (sampled sites) are adjacent to each other. Sampled water sources such as boreholes had a maximum depth of 105 m, as its less than the minimum depth of local groundwater flow system, the flow direction has a similar pattern to surface drainage.

3.5 Conclusion

The study was done to ascertain hydro-chemical characteristics of Lake Duluti and to assess lake-groundwater interactions. Hydro-chemistry data reveal that, Lake Duluti water is generally alkaline characterized by pH values between 8.6 and 9.3. Alkalinity and hardness were low indicating freshness of the lake water. Low EC and TDS reflected low concentration of TDS probably due to limited interaction between lake water and rocks and lake water is moderately hard, ranging from 60-120 mg/l (EPA). The abundance of major cations and anions in lake water is in the following order $Na^+>Ca^{2+}>K^+>Mg^{2+}$ and $HCO_3^->Cl^->F^->SO_4^{2-}>NO_3^-$. In all lake water samples taken during dry and wet seasons, Na^+ was the prevalent cation while HCO_3^- was the prevalent anion. Accumulated of Na^+ is due to evaporation thus probably, there is Lake Groundwater interaction influenced by ion exchange and mineral dissolution. The concentrations of ions into the lake water are influenced by ion exchange, mineral dissolution and anthropogenic activities. The dominant hydro-chemical facies is $Na\text{-}HCO_3$ water type for all water samples in Lake Duluti, while $Ca\text{-}HCO_3$ and $Ca\text{-}Na\text{-}HCO_3$ type were present in springs and boreholes, respectively during dry and wet seasons. The facies are caused by the influence of geogenic factors including ion exchange, mineral solubility; mineral dissolution and evaporation. Results discussed above for water chemistry shows that there is lake groundwater relation, as recharge through the aquifer takes place locally and hence probably groundwater recharges the lake.

CHAPTER FOUR

LAKE DULUTI ISOTOPIC WATER BALANCE AND LAKE-GROUNDWATER RELATIONSHIP

4.1 Summary

Water balance approaches were used to estimate surrounding ground-water exchange with Lake Duluti and addressing the role of groundwater on lake hydrological system. Due to increase in water demand for the Arusha city, Lake Duluti has been enmarked as an alternative source of water supply. However, as it’s a crater lake, there is high possibility of lake-groundwater exchange but the hydrological system of the lake is poorly understood. Hence there was a great need of studying the lake to ascertain if it can be used for water supply and to know its relation to surrounding groundwater sources.

Lake Duluti and surrounding groundwater sources were sampled during dry and wet season, for determination of the stable isotopes composition of oxygen and hydrogen (^{18}O and ^{2}H). In the laboratory, water samples were analyzed by the TC/EA-MS (High temperature conversion elemental analyzer-mass spectrometry) by injecting 0.1 ml of the sample into the helium carrier gas through a heated septum using a microliter syringe. Isotope results and theoretical consideration were used to perfome lake water balance and quantifying lake-groundwater exchange.

The isotopic composition $\delta^{18}O$ of lake water averaged 6.1‰ while that of well/boreles and spings averaged -1.2‰ and -2.1‰ respectively. Similarly, the δD of lake water averaged 24.2‰ while that of well/boreholes and spings averaged -12.9‰ and -12.2‰ respectively. Water balance calculations reveals that groundwater inflow to the lake is approximately 2 430 960 m^3/yr while discharge from the lake to groundwater is 2 902 620 m^3/yr. The lake is recharged through precipitation by 612 000 m^3/yr. Based on this findings from the study which showed that there is negative groundwater flow of 471 660 m^3/yr.

The results indicated that groundwater plays a role on the lake hydrological system, and the lake is fed by groundwater as compared to precipitation and surface runoff. The isotopic compositions of sampled lake water indicated high rate of evaporation while water samples from boreholes indicated that, there is limited evaporation of water as they are recharged through faults/ joints. However, results of the water balance calculation showed that the net ground-water outflow occurs from the lake. Water balance calculations shows that there is

more groundwater outflow than inflow and therefore remain as a base information for citing of boreholes in the area so as to maintain the state of the lake or groundwater aquifers.

4.2 Introduction

The stable isotopes of hydrogen (δ^{2}H) and oxygen (δ^{18}O) in water have long been used as naturally occurring tracers to assess sources, age and flux of water in the surface and groundwater resources (Gibson & Edwards, 2002; Russell & Johnson, 2006; Wolfe *et al.,* 2007; Wassenaar *et al.,* 2011).

Lake Duluti is one of the least studied crater lakes as little is known on its hydrology. With increase in water demand from surrounding villages and Arusha city there is need ensuring adequate supply throughout the year including during dry seasons. Lake Duluti has been suggested as an alternative source of water supply for Arusha city, hence there was a great need of ascertaining its source of water. Stable isotopes (δ^{18}O and δD) have been used as tracers have successfully been used to investigate hydrologic system of crater lakes such as Lake Challa, and Lake Mbaka but not in Lake Duluti.

Small crater lakes often have some groundwater influence but there are few studies done to emphasize the role of groundwater on the lake state (Ayenew, 1998). Stable isotope data, hydrological data and water balance have been used to constrain the physical hydrology of the lake, and particularly quantifying lake water inflow and outflow. Evaporation leads to lake change in isotopic composition of water and hence the stable isotopes method are used for determining water balance.

Water balance approaches were used to estimate groundwater exchange with L. Duluti and addressing the role of groundwater on lake hydrological system. The lake and surrounding groundwater sources were sampled for determination of the stable isotopes composition of oxygen and hydrogen (^{18}O and ^{2}H). Morever, theoretical considerations and water balance equations have been used to estimate lake water inflow and outflow and ascertaining lake-groundwater relation. According to Craig (1961), the seasonal co-variations between the ^{2}H and ^{18}O content of rain water results in a distinct local meteoric water line (LMWL) relationship which can be linked to ground and surface water resources.

Application of environmental isotopes is of importance as it reveals useful information about source and the mixing processes of water from the different sources.This study determines the lake-groundwater relationship of L. Duluti and lakes water balance.

4.3 Theoretical considerations

Water balance and isotopic balance equations were used collectively to ascertain the contribution of groundwater to the hydrological state of L. Duluti. Water budget equation for a closed lake can be estimated using the Sacks, Swancar *et al*. (1998) equation as shown in equation 1.

$dV/dt = Gi + P + Si - Go - E - So = 0$ …………………..………….. (1)

Where;

V= Volume of water in the lake, t= Time, P= Precipitation, E= Evaporation, Gi= groundwater inflow to the lake, Go= Lake outflow to the ground, Si = surface water inflow and So = Surface water outflow.

Equation 1 can also be written as:

$Gi + P + Si = Go + E + So$ ………………………………..……… (2)

Taking into consideration of isotope mass balance of $\delta^{18}O$ and $\delta^{2}H$ for a closed lake (Krabbenhoft, 2004; Bowser *et al*., 1994), Equation 2 can be expressed as shown in equations 3 and 4.

$\delta_{gi}Gi + \delta_{p}P + \delta_{p}KP = \delta_{go}Go + \delta_{E} E + \delta_{L}So$ for $\delta^{18}O$ ………….. (3)

$\delta_{gi}Gi + \delta_{p}P + \delta_{p}KP = \delta_{go}Go + \delta_{E} E + \delta_{L}So$ for $\delta^{2}H$ …………..… (4)

Where;

KP= total rainfall that is converted to runoff, K= Runoff coefficient, estimated based on field slope (Ayenew, 1998), δ_L=Isotopic compositionof lake water, δ_{gi} = Isotopic composition of groundwater inflow to the lake, δ_p=Isotopic composition of precipitation, δ_E=Isotopic composition of evaporation, δ_{go}=Isotopic composition of lake water outflow to the ground.

Slope of the area surrounding the lake has been determined from DEM using ArcGIS 10.2 as indicated in Fig. 11 and the side of possible runoff has been determined by SWAT as shown in Fig. 12. L. Duluti, a crater lake with its catchment confined by the crater walls, with no surface inlets or outlets, it is assumed to have negligible or no surface runoff and hence $S_o = 0$ as in Fig. 12 below. For water under Isotopic steady state condition, isotopic composition of water recharging the ground from the lake is the same as that of the lake (Kebede, 2006; Ayenew *et al.*, 2004) ($\boldsymbol{\delta_{go} = \delta_L}$).

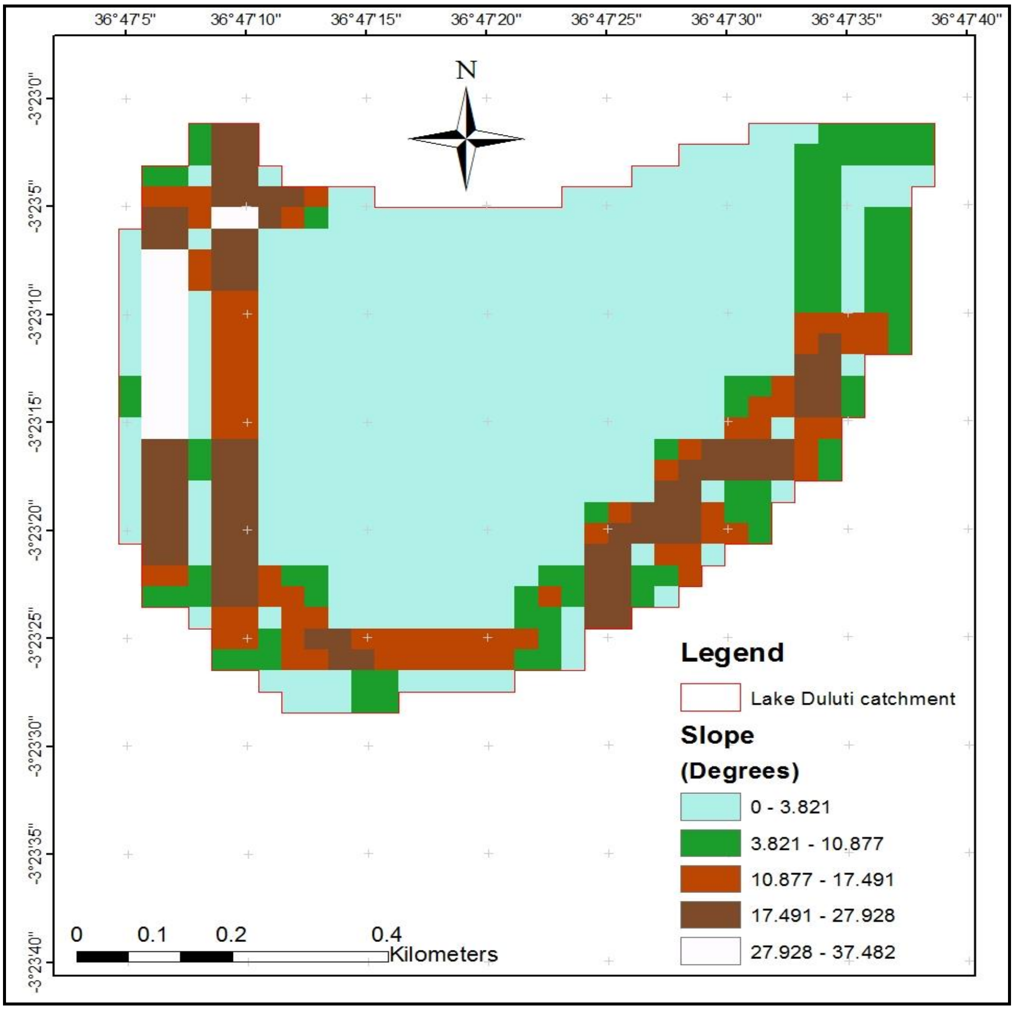


Figure 11: Slopes around Lake Duluti catchment

From the theories and assumptions above,

Equations 3 and 4 become;

For $\delta^{18}O$; $\delta_{gi}Gi + \delta_p P + \delta_p KP = \delta_L Go + \delta E\ E$ ………….. (5)

For $\delta^{2}H$; $\delta_{gi}Gi + \delta_p P + \delta_p KP = \delta_L Go + \delta E\ E$ ………….. (6)

Isotopic composition of evaporated water is derived from the assumption that, isotopic composition of the lake is the sum of isotopic composition of groundwater inflow to the lake, precipitation and evaporation.

$\delta_{gi} + \delta_p + \delta E = \delta_L$ ……………………….. (7)

Hence, $\delta E = \delta_L - \delta gi - \delta p$ …………...…..(8)

Final Equations for L. Duluti Isotopic water balance;

For $\delta^{18}O$; $\delta_{gi}Gi + \delta_p P + \delta_p KP = \delta_L Go + (\delta_L - \delta gi - \delta p)E$ ………….. (9)

For $\delta^{2}H$; $\delta_{gi}Gi + \delta_p P + \delta_p KP = \delta_L Go + (\delta_L - \delta gi - \delta p)E$ ………….. (10)

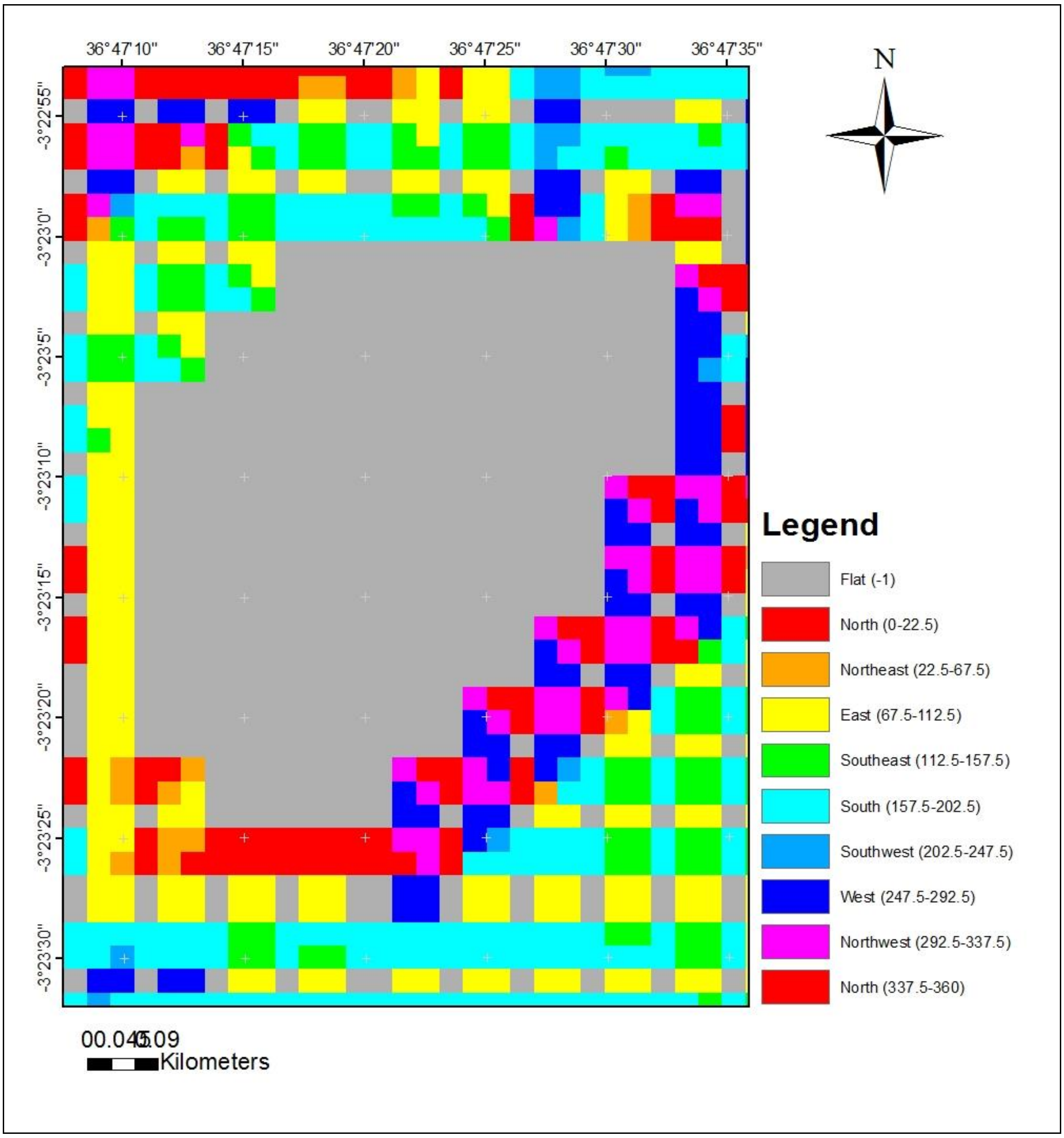


Figure 12: Runoff aspects around Lake Duluti

4.4 Results and discussion

Isotope analysis results of the sampled lake, rainfall and groundwater during dry and wet season are presented in Tables 6 and 7. Sampled water bodies for $\delta^{18}O$ Vs $\delta^{2}H$ are plotted with respect to the Local Meteoric Water Line (LMWL) as shown in Fig. 13. Local Meteoric Water Line (LMWL) data were obtained from the International Atomic Energy Agency (IAEA) for different areas of Tanzania. The Global Meteoric Water Line (GMWL) was generated based on the worldwide scale relationship revised by Rozanski (1993) with respect to the sampled isotopic composition data and relative to Standard Mean Ocean Water (SMOW). The points clustered around the GMWL show significant rainfall recharge.

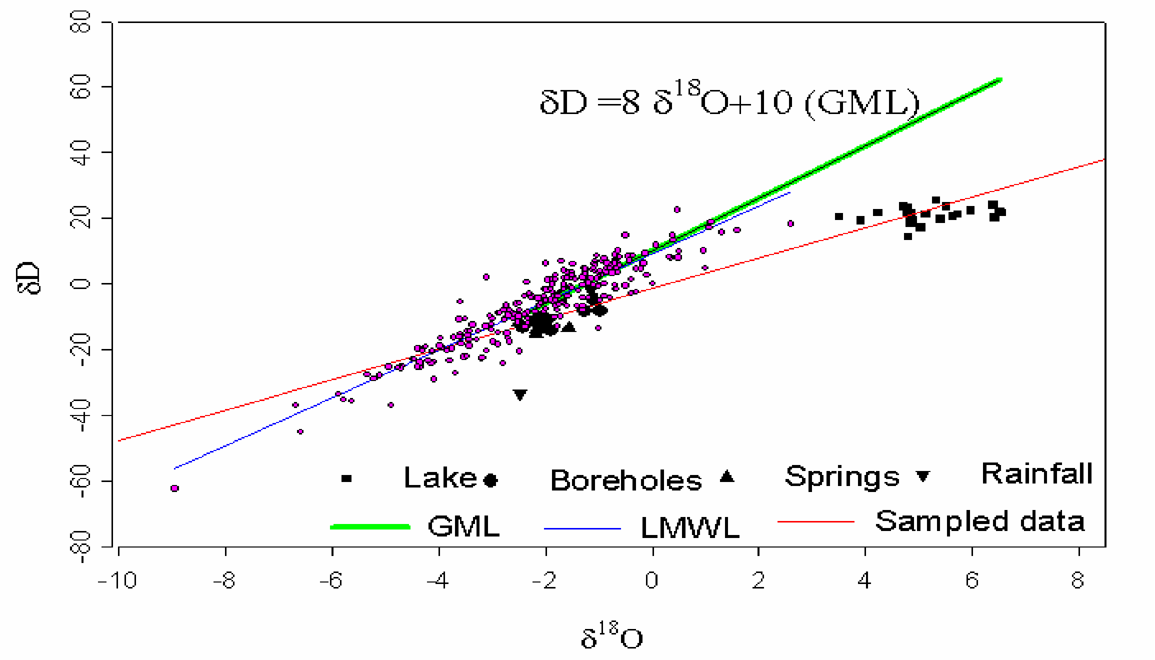


Figure 13: Plot of $\delta^{18}O$ Vs $\delta^{2}H$ of water samples with respect to the Local Meteoric Water Line (LMWL)

Isotopic compositions of sampled lake water lies to the upper right of the LMWL indicating high rate of evaporation. Water samples plotted close to the LMWL indicate that, there is limited evaporation of water (Yuan, 2011). Water falling outside the LMWL indicates the presence of evaporation, this is due to the fact that evaporation-induced isotopic fractionation and cause deuterium enrichment in water vapor and subsequently an isotopic enrichment of ^{18}O/ ^{16}O relative to D/H in lake water Evaporation effects and variation of temperature of precipitation contributed to some variability among samples.

Groundwater sources appearing concentrated to the left of local meteoric water line (LMWL) are indicative of no evaporation occourance during recharge either at the surface or within the soil zone. The range of δ-values Fig. 13 decreases from precipitation to lake water to groundwater. The isotopic composition of each of the water types and their significance is indicative of groundwater- surface water interaction as discussed below.

4.4.1 Results of isotopes analysis

Table 8: Stable isotopes compositions of lake and groundwater for the dry season

No.	Sample No.	Sample Site	EC(µS/cm)	$\delta^{18}O$	δD
		Lake Duluti			
1	LD1-S	Lake Pt A, surface	565	5.7	23.6
2	LD1-1.5	Lake Pt A, 1.5 m	548	5.5	19.1
3	LD1-4	Lake Pt A, 4m	569	5.1	25.7
4	LD2-S	Lake Pt B, surface	540	6.4	25.5
5	LD2-1	Lake Pt B, 1m	524	6.3	22.7
6	LD2-2	Lake Pt B, 2m	545	6.3	24.7
7	LD2-3	Lake Pt B, 3m	535	6.9	24.6
8	LD2-4	Lake Pt B, 4m	552	6.5	24.2
9	LD2-5	Lake Pt B, 5m	555	6.5	24.0
10	LD2-6	Lake Pt B, 6m	568	6.2	21.6
11	LD2-6.5	Lake Pt B, 6.5m	570	6.2	20.7
12	LD3-S	Lake Pt C, surface	540	6.0	24.9
13	LD3-1.5	Lake Pt C, 1.5m	540	6.1	25.0
14	LD3-3	Lake Pt C, 3m	538	6.6	26.4
15	LD4-S	Lake Pt D, surface	537	5.7	28.0
16	LD5-S	Lake Pt E, surface	536	5.0	27.0
		Groundwater Sources			
17	PPBH	Patandi P. Borehole (↑)	458	-2.4	-15.1
18	MHBH	Meru H. Borehole(↑)	346	-1.2	-12.9
19	MASP	Makisoro Spring (↑)	384	-2.4	-13.3
20	TBB1	Tengeru Borehole 1(↑)	337	-0.5	-13.3
21	TBB2	Tengeru Borehole 2(↑)	546	-0.5	-13.6
22	RCBH	Roman Borehole(↑)	459	-1.2	-16.7
23	DSBH	Duluti Sec Borehole(↑)	412	-1.6	-15.9
24	LTSP	Lita Spring(↓)	377	-2.8	-12.6
25	NMB1	NM-AIST Borehole 1(↓)	823	-0.6	-7.6
26	NMB2	NM-AIST Borehole 2(↓)	885	-1.2	-6.7
27	CDBH	CDTI Borehole(↓)	677	-1.7	-12.4
28	CDSP	CDTI Spring(↓)	549	-1.2	-10.9

Where; (↓) -, (↑) – indicate Downstream and Upstream relative to lake Duluti, respectively

Table 9: Stable isotopes compositions of lake, groundwater and rainfall during wet season

No.	Sample No.	Sample Site	EC(µS/cm)	$\delta^{18}O$	δD
		Lake Duluti			
1	LD1-S	Lake Pt A, surface	646	5.4	19.9
2	LD1-1	Lake Pt A, 1m	516	4.7	23.6
3	LD1-2	Lake Pt A, 2m	520	4.9	19.4
4	LD1-3	Lake Pt A, 3m	525	3.9	19.5
5	LD2-S	Lake Pt B, surface	541	5.1	21.3
6	LD2-1	Lake Pt B, 1m	511	4.8	14.5
7	LD2-2	Lake Pt B, 2m	515	4.8	18.3
8	LD3-S	Lake Pt C, surface	511	4.8	21.7
9	LD3-1	Lake Pt C, 1m	511	4.8	23.3
10	LD3-2	Lake Pt C, 2m	512	4.2	21.7
11	LD3-3	Lake Pt C, 3m	520	3.5	20.5
12	LD3-4	Lake Pt C, 4m	527	5.5	23.7
13	LD3-5	Lake Pt C, 5m	551	5.0	17.2
14	LD3-6	Lake Pt C, 6m	568	4.8	21.6
15	LD3-7	Lake Pt C, 7m	560	4.8	20.6
16	LD4-S	Lake Pt D, Surface	510	5.3	25.6
17	LD4-1	Lake Pt D, 1m	511	5.6	20.6
18	LD4-2	Lake Pt D, 2m	525	5.7	21.3
19	LD5-S	Lake Pt E, surface	511	6.5	21.9
20	LD5-1	Lake Pt E, 1m	511	6.4	20.2
21	LD5-2	Lake Pt E, 2m	512	6.4	24.2
22	LD5-3	Lake Pt E, 3m	519	6.0	22.4
23	LD5-4	Lake Pt E, 4m	557	6.2	21.7
		Groundwater sources			
24	PPBH	Patandi Borehole(↑)	468	-2.4	-13.3
25	MHBH	Meru H. Borehole(↑)	376	-1.9	-14.3
26	MASP	Makisoro Spring(↑)	364	-2.1	-12.9
27	CASP	Carmatec Spring(↑)	196	-2.2	-13.9
28	SASP	Saibala Spring(↑)	277	-2.2	-15.0
29	TBB1	Tengeru Borehole 1(↑)	462	-1.0	-8.3
30	TBB2	Tengeru Borehole 2(↑)	466	-1.3	-8.4
31	RCBH	Roman Borehole(↑)	468	-2.1	-10.4
32	DSBH	Duluti S. Borehole(↑)	435	-2.2	-11.6
33	LTSP	Lita Spring(↓)	402	-1.6	-13.5
34	NMB1	NM Borehole 1(↓)	830	-1.1	-4.8
35	NMB2	NM Borehole 2(↓)	888	-1.7	-3.9
36	CDBH	CDTI Borehole(↓)	682	-2.0	-10.9
37	CDSP	CDTI spring(↓)	565	-2.5	-11.7
	Rainfall				
38	Rain 1	Close to the lake		-1.2	-1.6

Where; (↓) -and (↑) - indicate Downstream and Upstream relative to lake Duluti, respectively

The results above (Table 6 and Table 7) are in **δ** notation in per mil (‰) versus SMOW; reproducibility is better than 0.3 and 3‰ for $\delta^{18}O$ and δD, as per the standard sample with respect to the water samples analysed .

Lake surface temperature, evaporation of lake water and precipitation were considered to be homogenous due to climatic and environmental conditions of the sampled area. An annual evaporation (E) of 1 700 mm/year was recorded at Arusha Airport, some 17 km west of Lake Duluti. The average annual precipitation (P) of approximately 1012 mm/yr was recorded at Tengeru, about 1 km from Lake Duluti (Tanzania Meteorological Agency). Lake average surface temperature (T) during sampling was 25.08 °C, with small variations with depth and seasons.

The isotopic compostions of oxygen and hydrogen ($\delta^{18}O_L$ and δ^2H_L) for lake water ranged from 3.5 to 6.9 ‰ for $\delta^{18}O$ and 14.5 to 28.0 ‰ for δ^2H. It averaged 6.1 ‰ for $\delta^{18}O$, 24.2 ‰ for δ^2H in dry season and 5.3 ‰ for $\delta^{18}O$, 21.1 ‰ for δ^2H for wet season respectively (Fig. 13, Tables 6 and 7). Similarly, the isotopic compositions of these two parameter for rainfall averaged -1.2 ‰ for $\delta^{18}O_P$ and -1.6 ‰ for $\delta^2H_{P.}$ Furthermore, the isotopic compositions for oxygen and hydrogen for surrounding groundwater sources ($\delta^{18}O_G$ and δ^2H_G) averaged -1.4 ‰ for $\delta^{18}O$, 12.4 ‰ for δ^2H in dry season and -1.9 ‰ for $\delta^{18}O$, -10.9 ‰ for δ^2H for wet season, respectively (Tables 1 and 2).

4.4.2 Isotopes and water balance calculations

Water balance for L. Duluti was calculated from the Isotopic calcuations as shown below:

Table 10: Water balance calculations

Calculations	**Results**
Lake Duluti water balance equations as per the theories discussed above ▪ From equation 5 and 6 For $\delta^{18}O$; $\delta_{gi}Gi + \delta_pP + \delta_pKP = \delta_LGo + \delta E\ E$ ………..….. (5) For $\delta^{2}H$; $\delta_{gi}Gi + \delta_pP + \delta_pKP = \delta_LGo + \delta E\ E$ …………... (6) ▪ Isotopic composition of evaporation For $\delta^{18}O$; $\delta E = \delta_L - \delta_{gi} - \delta_p = 5.2 - (-1.9) - (-1.2) = 8.3$ For $\delta^{2}H$; $\delta E = \delta_L - \delta_{gi} - \delta_p = 21.1 - (-10.9) - (-1.6) = 33.6$	$\delta^{18}O$; $\delta E = 8.3$ $\delta^{2}H$; $\delta E = 33.6$
Substituting all parameters to equation 5 and 6 **For** $\delta^{18}O$; $\delta_{gi}Gi + \delta_pP + \delta_pKP = \delta_LGo + \delta E\ E$ $(-1.9Gi) + (1021*-1.78) + (-1.78*0.3*1021) = (5.3\ G_o) +$ $(1700*8.3) - 1.9Gi - 5.2Go = 17{,}458.2$ ……………………. (9) **For** $\delta^{2}H$; $\delta_{gi}Gi + \delta_pP + \delta_pKP = \delta_LGo + \delta E\ E$ $(-1.9\ Gi) + (-1.34*1021) + (-1.37*0.3*1021) = (21.1G_o)$ $+(1700*33.6) - 10.9Gi - 21.2Go = 58{,}397.73$ ……………. (10) Where K is the Runoff coefficient= 0.3, characterized by slope ranging 0-3.8% and clay and silt soil type (DEM) Solving equation 9 and 10 simultaneously; G_i= 4051.6mm/yr and G_o= 4733mm/yr	G_i = 4051.6mm/yr G_o=4733mm/yr
Estimated groundwater inflow to the lake estimated Gi= G_i*Surface Area =4.051m *0.6km^2 =2,430,960m^3/yr	Water recharging lake from the ground= 2,430,960m^3/yr
estimated lake outflow to groundwater estimated G_o= G_o*Surface Area =4.837 *0.6km^2 =2,902,620m^3/yr	Water recharging the ground from lake = 2,902,620m^3/yr
estimated precipitation recharging the lake =Precipitation *Surface area of the lake =1,021mm*0.6km^2 =612,600m^3/yr	Precipitation recharging the lake =612,000m^3/yr
Net Groundwater flow Gnet = Gi – Go Gnet= 2,430,960m^3/yr - 2,902,620m^3/yr Gnet= -471,660 m^3/yr	Gnet=-471,660 m3/yr

Net groundwater flow is negative implying that the net ground-water outflow occurs from the lake, and this value can be considered to be the minimum amount of ground-water outflow in the lake’s water budget. However, slightly decrease in lake water level which was observed for a number of years is probably attributed by the continuous exchange of water masses by the lake and groundwater.

4.4.3 Isotopic variability and groundwater-surface water interaction

Mean isotopic compositions of lake water were 6.1±0.3‰ for δ^{18}O and 24.2±1.2‰ for δ^{2}H during dry season and 5.2±0.2‰ for δ^{18}O and 21.1±1.1‰ for δ^{2}H during dry and wet season, respectively. The lake is in the state of evaporation with respect to the present day precipitation as it is enriched with heavy isotopes. Isotopic composition of water sampled showed that the lake is more enriched than groundwater sources and rainfall, due to evaporation.

Groundwater sources are less enriched than the lake and their isotopic composition in the study area ranged from -0.5 to -2.8‰ for δ^{18}O and -3.7 to -6.7‰ for δ^{2}H. Results show some variation in isotopic composition of sampled groundwater, probably due to differences in sources (springs, boreholes), different sampled locations and temporal variations of recharge. There is little or no evaporation in groundwater as these are recharged through faults/ joints as compared to the lake, because its surface water is exposed to the atmosphere. Sampled rainfall close to the lake had isotopic composition of -1.2‰ for δ^{18}O and -1.6‰ for δ^{2}H. Results also shows that isotopic composition of water samples from upstream and downstream did not show any specific trend suggesting that the water sources recharging the lake is not from a specific elevations.

There is a slightly variation in the oxygen isotopic composition of Lake water with seasons and depth indicating that the lake is to some extent not isotopically mixed (Fig. 14). Most of the lake sampled sites showed decrease of oxygen isotopic composition with depth as evaporation on the lake surface leads to increase in δ^{18}O. Evaporation from the lake influence surface water to be more isotopically enriched.

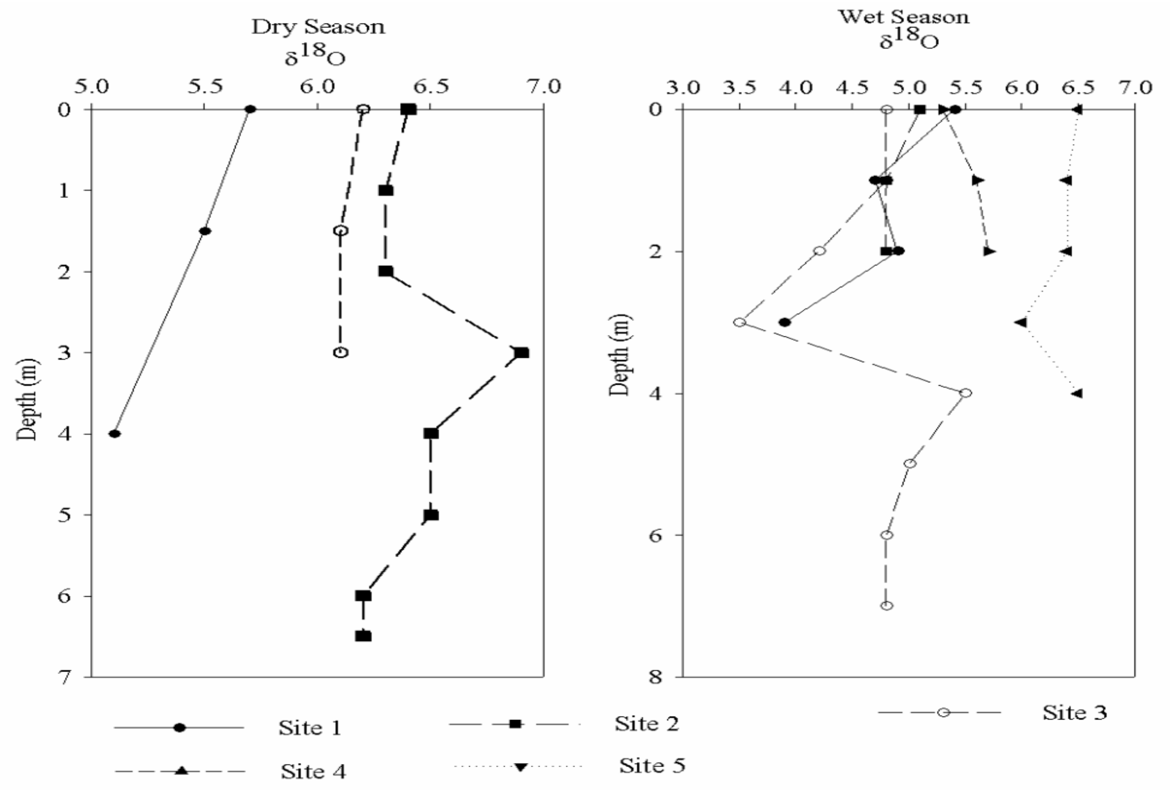


Figure 14: Trend of oxygen isotopic composition with depth in Lake Duluti

4.4.4 Groundwater estimation using two components mixing equation

Two component mixing equations has been used to ascertain the mixing of lake water and groundwater and to estimate the relative contribution.

Let;

δ_{Ls}- Isotopic composition of lake surface water

δ_G- Isotopic composition of groundwater

f_L- Fraction of lake water

f_G- Fraction of groundwater

$1= f_L + f_G$ ……………………….(i)

$\delta mix= \delta_{Ls}* f_L + \delta_G* f_G$ …………(ii)

But $1 – f_L = f_G$ and hence;

$\delta mix= \delta_{Ls}* f_L + \delta_G*(1- f_L)$……....(iii)

$\delta mix – \delta_G = \delta_{Ls}* f_L - \delta_G* f_L$

$f_G= \frac{\delta mix - \delta G}{(\delta Ls - \delta G)}$ …………(iv)

From the Isotopic composition data for $\delta^{18}O$; δ_{Ls} =5.5 and δ_G= -1.9 and the isotopic composition of mixed water (lake-groundwater), δmix is assumed to be the isotopic composition of lake water minus that of precipitation, groundwater and evaporation, as its proved by water balance calculation that the lake is recharged by groundwater.

From equation (iv);

$f_L = \frac{0.1 - (-1.9)}{5.5 - (-1.9)}$

$f_L = 0.27$

From equation (i),

$f_G = 1 - f_L = 1 - 0.27 = 0.73$

$f_L = 0.73$

Therefore fraction of groundwater is 0.73, which shows that groundwater contributes to 73% of lake water. This shows that groundwater play a role in lake Duluti, and it does have significant difference with the water balance results which showed groundwater contributes 80% of lake water.

Fractionation factor of evaporation is obtained from the Rayleigh equation;

$R = R_o f^{\alpha - 1}$ …………………………………….. (i)

Where by;

R_o= Initial isotopic ratio of the original substrate

R= Instantaneous remaining ration

f = Fraction of initial substrate

α= fraction factor

From the component mix equation; $1 = f_R + f_L$ ………..(ii)

Equation (i) can be written as;

$\ln (R/ R_o) = (\alpha - 1)f$ ……………………………….(iii)

Hence the Fractionation factor $\alpha = \{\ln (R/ R_o) + f_R \}/ f_R$ ………(iv)

The initial isotopic ratio of the original substrate is equal to the oxygen isotopic composition of precipitation and the Instantaneous remaining ration is the oxygen isotopic composition of lake surface water, substracting composition of groundwater and evaporation as they have affected the lake water composition.

Therefore R= $\delta_L - \delta_G - \delta_E$ = 5.3- (-1.9) + 8.3= -1.1 , R_o= -1.2 and

f_R= (lake surface area * precipitation) = 0.6km^2 *1021mm/yr =612,600m^3/yr

On substituting the above data to equation (iv)

α={ln (-1.1/ -1.2) + 612,599}/ 612,599

α = 0.99

Fractionation factor of evaporation is 0.99 indicating that slightly fractionation as precipitation falls to the lake .

4.5 Conclusion

Water balance is vital on determing hydrological system of Lake Duluti. The isotopic compositions of sampled lake water indicated high rate of evaporation. Water samples from boreholes indicated that, there is limited evaporation of water as they are recharged through faults/joints as compared to the lake, as its surface water is exposed to the atmosphere. However, results of the water balance calculation showed that the net ground-water outflow occurs from the lake and groundwater plays significant role in the hydrological state of the lake. Isotopic composition of water sampled showed that the lake is more enriched than groundwater sources and rainfall, due to evaporation and the amount of groundwater outflow probably is accountable for the difference in the L. Duluti water salinity. Based on this findings from the study more groundwater outflow than inflow and therefore remain as a base information for citing of boreholes in the area so as to maintain the state of the lake or groundwater aquifers.

CHAPTER FIVE

GENERAL DISCUSSION, CONCLUSION AND RECOMMENDATIONS

5.1 General discussion

The pH of the Lake, is mildly alkaline, a result of natural processes including interaction between lake/groundwater and alkaline volcanic rocks (Öberget *et al*., 2012). Decreasing trend of pH with depth in lake may be attributed to photosynthesis of phytoplankton and submerged plants, the respiration of organisms and decomposition of organic matter (Ajioka *et al*., 2014). Water temperature decreased with depth and lacked a sharp thermocline indicating lack of stratification. A difference of over 1 ^oC between surface and bottom water in the lake is an indication of groundwater input or flux to the lake, supported by the results of oxygen isotopes which showed a decreasing trend with depth. DO decreased with increasing depth during both the dry seasons attributed to high rate of oxygen during oxidation of descending organic matter.

Ion exchange influences the higher contribution of Na^+ than that contributed by Ca^{2+}. The dominance of Na^+ and HCO^{3-} ions in the lake indicates precipitation of Ca^{2+} as $CaCO_3$ (Anazawa, 2001). Higher concentration of K^+ in lake than groundwater sources probably due to evaporative cumulative effect or input of runoff from nearby farms where fertilizers are applied. Similarly, the evaporation process contributes to higher concentration of fluoride in lake than in the surrounding groundwater, the lake receives water from the ground with low concentration of F^-, which later accumulates as water evaporates. The concentration of NO_3^- in lake water was significantly lower ($p<0.01$) than in groundwater owing to minimum anthropogenic input or high primary productivity of macrophytes and phytoplankton. Elevated nitrate concentration (above 10 mg/l) was observed in some groundwater sources indicating possible pollution from agriculture activities and sanitation facilities.

Groundwater sources are less enriched than the lake and their isotopic composition ranged from -0.5 to -2.8 ‰ for $\delta^{18}O$ and -3.7 to -6.7 ‰ for δ^2H. Variation in isotopic composition of sampled groundwater is probably due to differences in sources (springs, boreholes), locations and temporal variations of recharge. There is little or no evaporation in groundwater as the isotope values of rainfall (-1.2 ‰ for $\delta^{18}O$ and -1.6 ‰ for δ^2H) are similar to those of groundwater. The observed general trend of decreasing with depth in $\delta^{18}O$ and δ^2H in both seasons suggests upward diffusion of water isotopically depleted most likely derived from groundwater aquifer. Two component mixing equations suggested that the relative contribution of groundwater to the lake which correspond with the water balance results which showed groundwater contributes 80 % of lake water indicating that groundwater play a role to the existence of the lake.

5.2 Conclusion

Lake Duluti is a fresh lake, generally alkaline, water is moderately hard, ranging from 60-120 mg/l (EPA). In all lake water samples taken during dry and wet seasons, Na^+ was the prevalent cation while HCO_3^{2-} was the prevalent anion. The dominant hydro-chemical facies is Na-HCO_3 water type for all water samples in Lake Duluti, while Ca-HCO_3 and Ca-Na-HCO_3 type were present in springs and boreholes, respectively during dry and wet seasons. Water chemistry also shows that lake-groundwater interaction is influenced by ion exchange and mineral dissolution. Isotopic results indicated high rate of evaporation in the lake. Lake Duluti is recharged by the groundwater as compared to precipitation and surface runoff. However, water balance calculations also reveals that groundwater plays significant role in the hydrological state of the lake. The results reveals that, there is more groundwater outflow than inflow, this information will be of assistance on citing of boreholes in the study area so as to maintain the state of the lake or groundwater aquifers.

5.3 Recommendations

The results provided gives the baseline for further study of the lake. Further research is recommended to investigate the possible direction of groundwater flow to the lake (mechanisms of lake recharge) and actual extent threat of use of boreholes surrounding the lake. Modelling interactions between groundwater and lake waters is also suggested. Public awareness on the importance of the lake is highly suggested and mitigation measures of illegal abstraction of water from Lake Duluti water.

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