

DYNAMICS OF WATER COMPOSITION IN THE SOUTH-EASTERN (SOKOTO)
SECTOR OF IULLEMMEDEN BASIN, NIGERIA, USING ISOTOPE AND HYDRO-
CHEMICAL TECHNIQUES

BY

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SEPTEMBER, 2016

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CHEMICAL TECHNIQUES

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU
BELLO UNIVERSITY, ZARIA

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD
OF
DOCTOR OF PHILOSOPHY DEGREE IN ENVIRONMENTAL ENGINEERING.

DEPARTMENT OF WATER RESOURCES AND ENVIRONMENTAL ENGINEERING,
FACULTY OF ENGINEERING
AHMADU BELLO UNIVERSITY,
ZARIA, NIGERIA

SEPTEMBER, 2016

DECLARATION

I declare that the work in this thesisentitled 'Dynamics of water composition in the South-Eastern (Sokoto) sector of Iullemmeden Basin, Nigeria, using isotope and hydro-chemical techniques'has been performed by me in the Department of Water Resources and Environmental Engineering. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other Institution.

Ogechukwu Jennifer Ette.....

Name of student

Signature

Date

CERTIFICATION

This thesis titled 'DYNAMICS OF WATER COMPOSITION IN THE SOUTH-EASTERN (SOKOTO) SECTOR OF IULLEMMEDEN BASIN, NIGERIA, USING ISOTOPE AND HYDRO-CHEMICAL TECHNIQUES by Ogechukwu Jennifer Ette meets the regulations governing the award of the degree of Doctor of Philosophy of the Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This thesis is dedicated solely to Charles. I. Chukwudolue, Michelle. C. Chukwudolue Roseline O.Etteh, my in-laws, the Etteh and Chukwudolue's family.

ACKNOWLEDGEMENTS

Specially, I thank Prof. C. A. Okuofu, Sir, you put your shoulder to the wheel, to ensure I was incorporated in the Nigeria Hydrological Services Agency (NIHSA) regional project to which this study keyed in to realize its main goal and you were interested in the study from the onset till now. Many thanks to my Project Supervisory Team comprising of Prof. C.A. Okuofu, Dr. D. B. Adie and Engr (Dr.) S.B. Igborofor their directions, constructive contributions and comments that led to the production of this final report. The critical comments of members of academic staff of Water Resources and Environmental Engineering (WREE) Department, ABU, Zaria, that have led to a better and more rigorous end product is well appreciated. I thank the team of WREE laboratory technicians who were supportive during the laboratory analysis of carbonate and bicarbonate ions.

I would like to express my sincere thanks to Nigeria Atomic Energy Commission(NAEC) for supporting this study by granting the researcher study leave. Specially, I acknowledge the moral support and persistent efforts of Prof. Agu (Commissioner Nuclear Power Plant Development Directorate (NPPD)), Mr. Uche Madu (Senior Colleague) and Mr. Chukwudi Anyawu (Senior Colleague) of International Atomic Energy Agency (IAEA) towards getting a fellowship grant to better aid the output of this study.

Gratefully, I acknowledge the cordial working relationships I have enjoyed with the members of staff of NIHSA, FCT, Abuja and specially Mr. S. U. Hussain, Mr.S. O. Okpara, and Mr. C. B. Ojo with whom I worked with during the field campaign exercise, and map design training exercises. The support given by Prof, S.A Alagbe in provision of academic materials and every onelse whose fruitful cooperation I enjoyed in realizing the goal of this study, is duly acknowledged.

Above all, I owe my life to God Almighty who used Prof O Benson as an instrument to channel my carrier in the right direction without which I would not have come this far, to you, I give all glory, honor and adoration. Prof. O. Benson, I also remain grateful to you, thank you, Sir.

ABSTRACT

The Sokoto Basin, (the South-Eastern sector of Iullemeden basin), located in Nigeria, consists of an aquifer system which is bi-layered with cretaceous Continental Intercalaire (CI) sedimentary deposit at the bottom, (Sokoto Group, Rima Group, Gundumi-Ilo Formation), by Continental Terminal (CT) Formation (Gwandu Formation) and surface water. The water of the basin is generally used for drinking, domestic, industrial and agricultural purposes. The water resources of the basin are being threatened by contamination, weak hydro-dynamic aquifer characteristics and sparse water quality data. Hydrochemical and isotope techniques have not really been applied to examine the water composition of the basin. In an attempt to bridge the gap in paucity of water quality data, hydro-chemical techniques and common environmental isotope signatures were applied to characterize the basin water composition. Eighty seven water samples consisting of eight surface water samples and seventy nine ground water samples were collected from the basin in July 2013 and April 2014; and analyzed for physico-chemical parameters (pH, Temp, EC, TDS, Ca, Mg, Na, K, F, B, Pb, Cr, Cd and Fe) and isotope constituents ($\delta^{18}\text{O}$, $\delta^2\text{H}$, ^3H). Hydrochemistry of major ions (Ca^{+2} , Na^+ , Mg^{+2} , K^+ , HCO_3^- , SO_4^{-2} , Cl) and common environmental isotopes ($\delta^{18}\text{O}$, $\delta^2\text{H}$, ^3H) were used to categorize the water resources of the basin into different water types. Heavy metals were subjected to further assessments and evaluation applying heavy metal index (MI) and heavy metal Degree of Contamination (CD) to find out the extent of metal contamination. The water quality for different uses was determined by assessment and evaluation of standard criteria. Three different water types were identified, calcium bicarbonate type (Ca- HCO_3); calcium sulphate type (Ca- SO_4); and sodium bicarbonate type (Na- HCO_3). The groundwater composition is largely controlled by dissolution of carbonate rocks, evaporite (gypsum) and cation-exchange of probably clay minerals. The isotope signature of the waters of the basin shows that the waters are made up of modern waters which are moderately depleted with $\delta^{18}\text{O}$ content (-6.59‰ to -3.20‰, mean = $-4.49 \pm 0.3\%$) and $\delta^2\text{H}$ content (-37.12‰ to -20.75‰, mean = $-27.26\% \pm 1\%$) compared with that of paleowaters (-7.72‰ to -6.84‰, mean = $-6.87 \pm 0.3\%$) and $\delta^2\text{H}$ content (-48.26‰ to -46.96‰, mean = $-47.13 \pm 1\%$). This indicates that an appreciable fraction of modern waters recharge CT and CI aquifer system of the basin. Also, there is recharge from evaporated waters of mainly surface water origin enriched with stable isotope signature with delta values of $\delta^{18}\text{O}$ (-3.52‰ to -1.05‰, mean = -2.89%) and $\delta^2\text{H}$ of (-17.65‰ to 6.75‰, mean = -9.79%). The basin surface water is considerably more

evaporated than the groundwater. The surface waters have generally low dissolved solid content and are due to the full exposure of the surface water to high atmospheric temperatures throughout the year. The unstable isotope ($\delta^3\text{H}$) signature confirms that the water composition of the basin consists of paleowater with extreme value of tritium content from 0.0TU to 0.5TU and of young water from 0.5TU to 4.5TU. Determining the suitability of waters for drinking, domestic and industrial purposes the mean concentrations of physico-chemical constituents in the water samples were compared to European Union (EU), United State Environmental Protection Agency (USEPA), World Health Organization (WHO), Bureau of Indian Standard (BIS) and Nigerian Industrial Standard (NIS). The results fall within permissible limits except for the heavy metals' concentrations in some wells located in urban areas that exceed the permissible limits most probably due to anthropogenic inputs. The metal index values indicate that the water quality in the studied areas fall within 'low class' and 'medium class' according to the classification of heavy metal water quality using the heavy metal index. Sodium Adsorption Ratio (SAR), Percent Sodium (Na %), Magnesium hazard and Residual Sodium Carbonate (RSC) results revealed that most of the sampled waters are suitable for irrigation. Generally, this study characterized the aquifer system of the basin on the bases of physico-chemical and isotopic features and ascertained the contamination status of the aquifers of the basin. Besides, it was able to establish based on the findings that contrary to earlier claims and beliefs, a considerable amount of modern water enters the Continental Intercalaire aquifer and the waters of the aquifers are related. The suitability of the waters of the basin for different uses was also established and was found to be useful in diversified applications. However, it is recommended that climate variability and soil assessment of the basin be carried out for contamination index determination. It is further recommended that the quantity of modern water recharging the aquifer system of the basin and age of the waters should be determined.

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LIST OF ACRONYMS

BIS	Bureau of Indian Standard
Cd	Cadmium
CD	Contaminant Degree
CERT	Center for Energy and Research Training
CI	Continental Intercalaire
CNESTEN	Centre National des Sciences et Technologies Nucléaires
CT	Continental Terminal
DEM	Digital Elevation Model
EU	European Union
FEPA	Federal Environmental Protection Agency
GEF	Global Environment Facility
GMWL	Global Meteoric Water Line
GNIP	Global Network of Isotopes in Precipitations
GPS	Global Positioning System
HDPE	High density polyethylene
IAEA	International Atomic Energy Agency
IAS	Illummeden Aquifer System

ICP-MS	Inductively Coupled Plasma Mass Spectrometry
JICA	Japan International Cooperation Agency
LMWL	Local Meteoric Water Line
Mbsl	Meters below sea level
Masl	Meters above sea level
MH	Magnesium Hazard
MI	Metal Index
MUSL	Multi-User Laboratory
NESREA	National Environmental Standards and Regulations Enforcement Agency
NIHSA	Nigeria Hydrological Services Agency
NIS	Nigeria Industrial Standard
OSS	Sahara and Sahel Observatory
Pmc	Percent modern carbon
RE	Reaction Error
RSC	Residual Sodium Carbon
SAR	Sodium Adsorption Ratio
SARDA	Sokoto Agricultural and Rural Development Authority
TDLAS	Tunable Diode Laser Spectrograph

TDS	Total Dissolved Solid
USEPA	United State Environmental Protection Agency
VPDB	Belmenide fossil from Pee Dee Limestone formation in USA
V-SMOW	Vienna Standard Mean Ocean Water
WHO	World Health Organisation
WREE	Water Resoureces and Environmental Engineering

DEFINITIONS

Absorption	Occurs, when sorbate enters the mineral structure, (Singhal and Gupta, 2010)
Adsorption	Is a process whereby molecule or ion is held at the solid surface, (Singhal and Gupta, 2010)
Altitude effect	is defined when precipitation progressively depletes in δ -values with increase in altitude, (Kumar, 2010)
Base exchange	Base or cation exchange occurs when an ion in solution gets sorbed to a surface and a similar charged ion is released leading to adsorption of cations on mineral surfaces, (Fitts, 2002; Hiscock, 2005; Singhal and Gupta, 2010)
Continental effect	the continental effect is observed in the precipitation, (Kumar, 2010).
Desorption	Desorption is the release of molecules and ions from the solid phase to the solute,(Singhal and Gupta, 2010).
Isotope	Is defined as atoms of an element having different number of neutrons (N) but same number of protons or electrons (Mazor, 2004).
Isotope effects	these are the differences in chemical and physical properties arising from variations in atomic mass of an element, (Hoefs, 2009)
Isotope Fractionation	Is the partitioning of isotopes between two substances or two phases of the same substance with different isotope ratios, (Mazor, 2010)
Latitude effect	At higher latitudes, precipitation tends to have more negative $\delta^{18}\text{O}$ values due to the strong relationship between $\delta^{18}\text{O}$ content and temperature. Seasonality effect is the Variation of δD and $\delta^{18}\text{O}$ due to change in season, (Kebede, 2012)
Sorption	Sorption involves mass transfer from the solution to the solid by adsorption or absorption, (Singhal and Gupta, 2010).
Potable water	Potable water is water fit for human consumption and domestic use, which is sanitary and normally free of minerals, organic substances, and toxic agents in excess or in reasonable amounts for domestic usage in the area served, and normally adequate in quantity for the minimum health requirements of the persons served, (Spellman, 2008).

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background of Study

In 1931, the phrase 'Iullemmeden Basin' was earlier defined by Radieras the Sedimentary Basin which extends from Mali and the Western boundary of the Republic of Niger through northern Benin Republic and northern Nigeria(Kogbe,1979) where it is referred to as 'Sokoto Basin', into eastern Niger (Fig. 1.1).

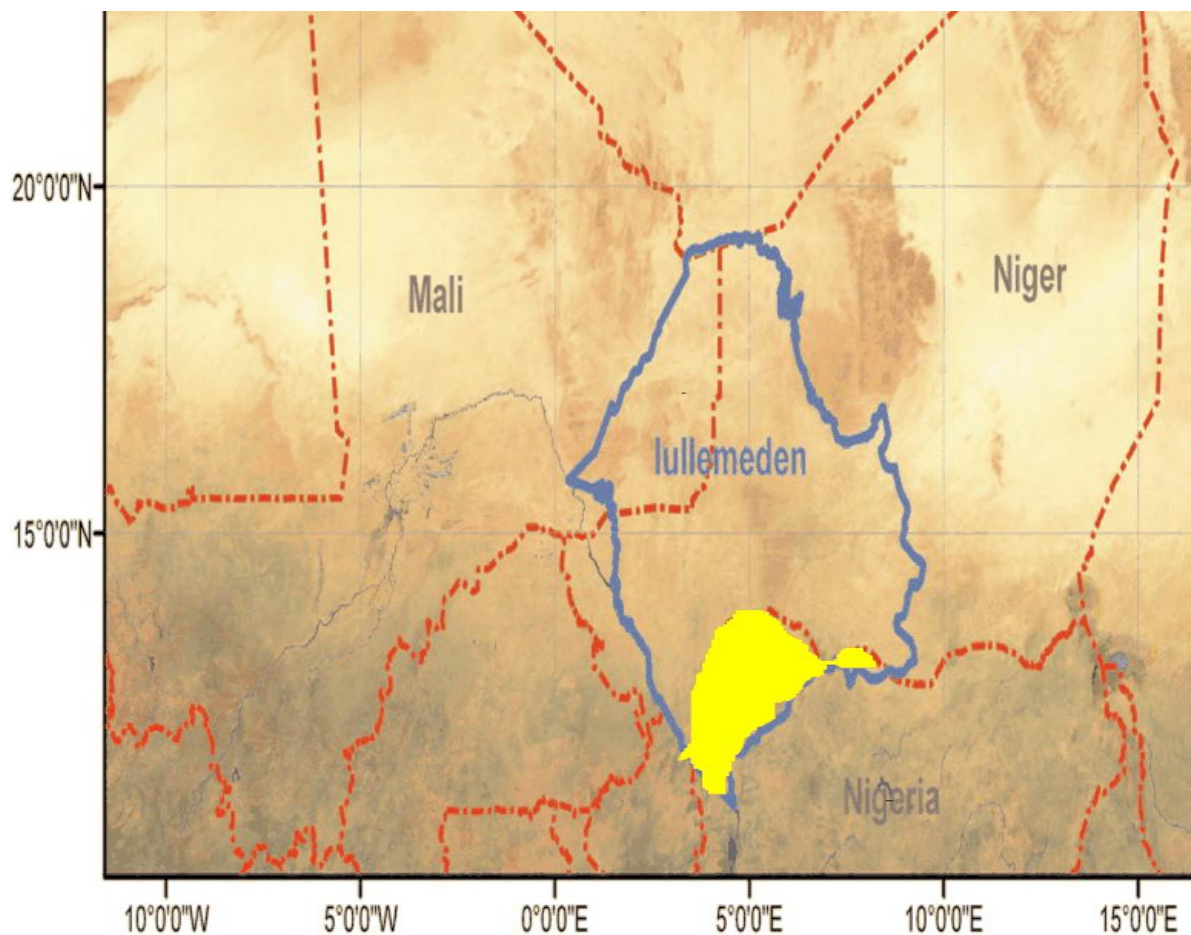


Figure 1.1: Location of Sokoto Basin in Iullemmeden Basin (Modified from: OSS, 2008)

It is located in the arid and semi-arid area of West Africa with the population of approximately 15million, which is projected to rise to 28 million in 2025 (GEF, 2003).The Iullemmeden Aquifer System (IAS) properties according to (GEF, 2003) is such that the depth

ranges between 1500 to 2000mbsl (with aquifer section below 250mbsl are not usually considered to take active part in modern hydrological cycle), the water level vary from 0 to 80m and transmissivity fall between 10^{-3} to 10^{-4} m²/sec. The recharge zones of the sedimentary deposit for IAS is in the northeast (in Niger) and northwest (in the Taoudeni basin in Mali) ridges, and in the south with input from the Rima River (or Goulbi de Maradi), and the Drainage zones are mainly the Niger River and the Rima River, one of its affluent (GEF, 2003; OSS, 2008 and AzTech, 2010).The aquifer system covers an area of 525,000km², with 31,000km² in Mali, 434,000km² in Niger and 60,000km² in Nigeria, where it is also known as Sokoto Basin. Sokoto Basin which covers Sokoto, Kebbi, Zamfara and parts of Kastina States in Nigeria is the area for this study.It stretches between latitudes 10° and 14° North and longitudes 3° and 7° east, as shown in the base map of the study location(Appendix, I).

The Basin lies in the sub-Saharan Sudan belt of West Africa in the area of savanna-type vegetation categorized as semi-arid. The Basin broadly covers an area underlain predominantly by crystalline rocks to the east and sedimentary terrain to the northwestern half according to Anderson and Ogilbee (1973). Similar to Iullemeden aquifer system, Sokoto Basin is multi-layered including a cretaceous Continental Intercalaire (CI) sedimentary deposit at the bottom (Gundumi-Ilo Formation) overlain by three layers of Continental Terminal (CT) Formations (Gwandu Formation, Sokoto Group and Rima Group), as shown in (Fig. 1.2). The Sokoto Group consist of three distinct sedimentary formations which includes: Gamba, Kalambaina and Dange Formations and Rima Group also consist of distinct Formations which include: Wurno, Dukamaje and Taloka Formations.

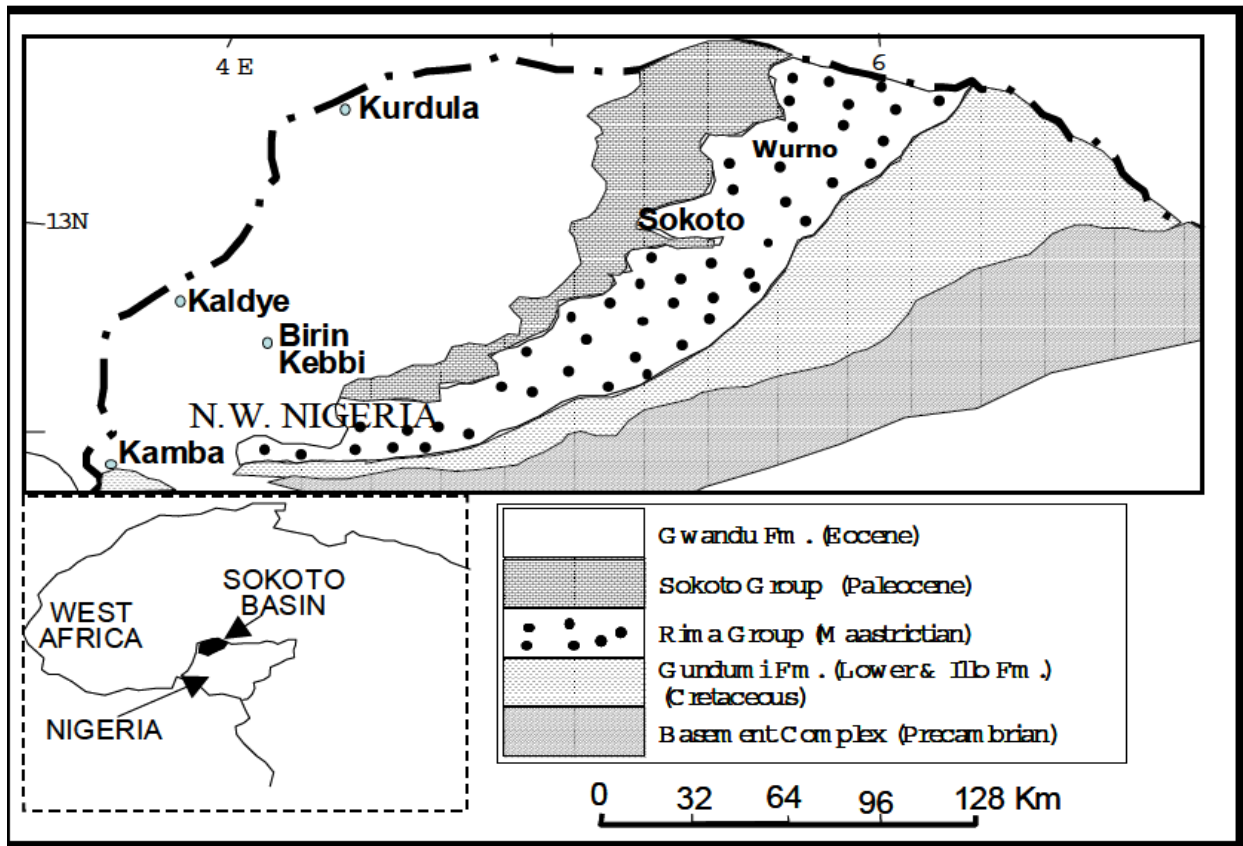


Figure 1.2: Geological Map of Sokoto Sedimentary Basin (Modified from AzTech, 2010)

Geomorphologically, the area is undulating with depressions due to Wadis and tributaries, with laterites and ironstones that characteristically cover the hills of the basin, (AzTech, 2010). The Sokoto and Rima Rivers are the principal drainage network, (Kogbe, 1979). The headwaters of the Sokoto and Rima rivers as well as their tributaries rise in pre-Cretaceous crystalline rock terrain east of the Sokoto Basin and flow west and south across the outcrop zones of the Gundumi-Ilo Formation, the Rima and Sokoto Groups, and the Gwandu Formation, (Anderson and Ogilbee, 1973). There are other tributaries to the main drainage networks which include Shella River, Bunsuru River, Gagere River, Kware River, among many others. Rainfall in this area percolates directly into the sandy soil or flows in minor tributaries where it infiltrates or evaporates and may eventually dry out during the peak of dry season. The major urban settlements in the area are: Sokoto, Birnin Kebbi, Gusau and Gwandu. There

are low-lying flood plains (Fadamas) which are used during the dry season for irrigated agriculture. The characteristic agricultural products are grains and vegetables. Dams like the Goronyo, Bakolori, Zobe, Shagari and Jibiya dams, (Okuofu, 2006) are identified reservoirs in the region. Traditionally, water supply in many rural settlements in the Sokoto Basin is based on rainwater, surface water and ground water.

The degradation of water quality has been identified as one of the major challenges of the basin by previous researchers. There is sparse data about water quality and existing data on the hydrodynamic aquifer characteristic from this region is weak (Okuofu, 2006). The Intercalary Continental, have little outcrop, are not easily renewed, some authors report that its non renewable and are thus threatened to mining exploitation. Presently, these water resources face the consequences of overexploitation such as decline of the piezometric level, degradation of water quality and the effects of climate change and variability (OSS, 2008). As such, this study focused on gap bridge in limited data on water quality in the basin. Groundwater, unless contaminated, is generally of better quality than surface water and in an effort to provide the population with safe, adequate, and sustainable water supply, the significant groundwater resources, have increasingly been exploited and contaminated. The recorded water quality issues in the basin are: high ground water salinity, high fluorine contents, pollution from agricultural sources, and infiltration of toxic chemicals and organic polluting waste from agro-industries. The contaminants may be due to mineral exploration for precious metals and petroleum in the region GEF(2003) and OSS(2008). This will have indirect impact on other riparian countries (transboundary aquifer). Therefore, need for sustainable water resources management of the Sokoto Basin through application of environmental Isotope in combination with hydrochemical technique to study the dynamics of water composition in the basin is vital. Numerous studies have been carried out in this Basin, including studies on geological

formations of the basin to water resources integration of the basin (Falconer, 1911; Raeburn and Tattam, 1930; Jones, 1948; Radier, 1957; Bell, 1961; Du-Preeze *et al.*, 1965; Anderson and Ogilbee, 1973; Kogbe, 1979; Oteze, 1989a; Adelana *et al.*, 2003; Alagbe, 2004; Okuofu, 2006; Sokona *et al.*, 2008; AzTech, 2010; Al-Gamal, 2011 and among many others) using mainly hydro-chemical approach. In this respect, environmental isotope in complementary with hydrochemical approach were applied in conducting this study. Isotope and related techniques are unique and effective tools for obtaining hydrologic information for a broad range of water resource management issues; timescale of hydrological events, identify the origin of water, renewal potential of an aquifer e.t.c. Therefore, in the present study, a joint application of hydro-chemistry and common environmental isotopes were applied to study the dynamics of the water composition of the aquifer in the basin in order to bridge the gap in sparse water quality data which will aid in making sound water planning decision for sustainable development.

1.2

Statement of Research Problem

The identified challenges of Iullemeden Aquifer System (IAS) reported by the previous researchers (GEF, 2003; Okuofu, 2006; OSS, 2008; Hearn, 2009; AzTech, 2010; NIHSA, 2012) can be grouped into three, which include- Decrease of water resources, Degradation of water quality, and Impacts of climate variability as stated earlier. Population growth with corresponding increase in demand for water has led to quantitative stresses on groundwater. Excessive extraction contribute to various undesirable effects, including: pumping cost increase, seawater intrusion (in Coastal areas) and poor-quality water from polluted aquifers, (Spellman, 2008). Severe depletion of groundwater resources is often compounded by a serious deterioration in its quality. According to Okuofu (2006), there is paucity of data about

water quality in the basin and the existing data on water quality and on hydrodynamic aquifer characteristics from this region is weak. OSS (2008), reported that groundwater pollution is one of the major risk in the basin. These stresses and their negative impacts in the long run may severely affect socio-economic developments such as degradation of the human condition, shut down of industries, progressive abandonment of the agricultural lands and high economic and environmental costs to future generations. Moreso, IAS is located in the earth's most vulnerable regions to climate change, desertification and drought, phenomena that threaten, among other things, the recharge of the aquifers (Fig. 1.3).

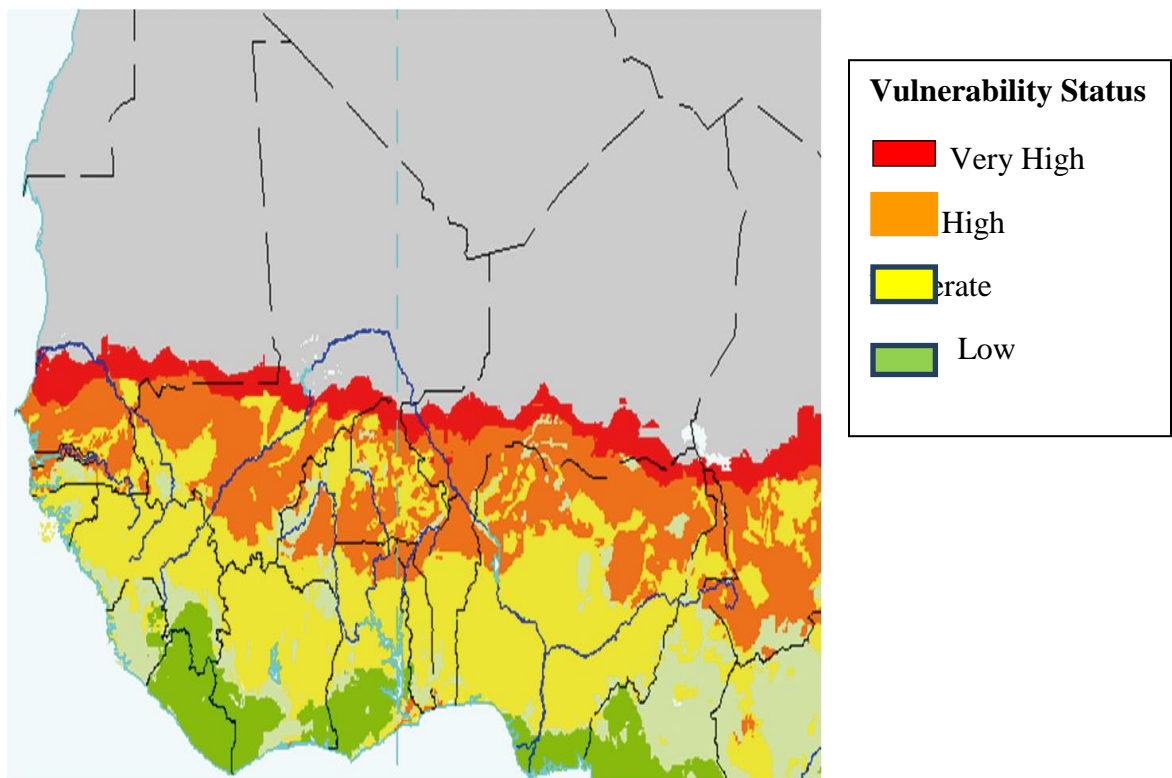


Figure 1.3: Climate change vulnerability map (Legend modified from OSS, 2008)

In order to contain these situations, there is need to fulfill present-day needs via ensuring the availability of quality water resources and for the wellbeing of future generations. This requires considering together all significant physical and environmental parameters, including

both surface and groundwater (Pennequim, 2008). In an attempt to contribute to the Sokoto Basin sustainable development, this study applies common environmental isotope inconjunction with hydrochemical approach to study the dynamic of water composition in the area.

1.3 Justification of Study

As human population continues to grow, regional conflicts over water, environmental degradation and human illness and death are on increase (Gleick, 1998); typical instances includes, two dozens children stricken with leukemia in Woburn; Storrs, Connecticut, where wells polluted by a landfill leachate were suspected of sickening and killing residents in nearby homes; Lead poisoning in Zamfara State, Northern Nigeria which was traced to the processing of Lead-rich ore, mined by artisans in the state for Gold extraction (Udiba *et al.*, 2013) etc.

Groundwater from the aquifers contains quality water (UN-W, 2008), however, the occurrence of groundwater contamination is a legacy of past and present land-use practices and poor controls on waste disposal. Many raw materials and chemicals have had a long history of usage before becoming recognised as hazardous. During this time, handling and waste disposal practices have frequently been inadequate. In the United states alone, the National Academy of Science (1994) reported that there are an estimated 300,000 to 400,000ha, hazardous waste sites in the United states. In Nigeria, Koko toxic waste episode was recorded in Delta State, in 1987. Arising from the Koko toxic waste episode, Federal Environmental Protection Agency (FEPA) was established through Decree 58 of 1988 and 59 (amended) of 1992 FEPA was then charged with the overall responsibility for environmental management and protection. Due to existing vacuum in the effective enforcement of environmental laws, standards and regulations in the country, National Environmental Standards and Regulations Enforcement Agency (NESREA), was established by 2007, (NESREA, 2011). Three years

after NESREA was established, cholera epidemic was declared in many states in Nigeria among which includes States covering Sokoto Basin (Sokoto, Zamfara, Kebbi), and also Lagos, Oyo and Plateau, (This Day Live, 2010). Innovation to long-term water planning and management that incorporate principles of sustainability and equity are required as such according to (Ogabiela *et al.*, 2011) thorough examination of physicochemical parameters of water is necessary.

Moreover, in Sokoto basin, Okuofu (2006) stated that there is paucity of data about water quality in the Basin. The use of Isotope technology was discovered in the nineteenth century. Though it has been applied vastly in the study of water in North Eastern Nigeria (Fig 1.4), it has not really been applied in hydrological studies in North Western Nigeria. Besides, a greater part of Rima and Sokoto Formations are still uncovered despite the limited application in Wurno irrigation scheme in Rima Formation. It is therefore vital to extend the application of isotope study over other parts of the basin and need to increase the water quality data in the basin.

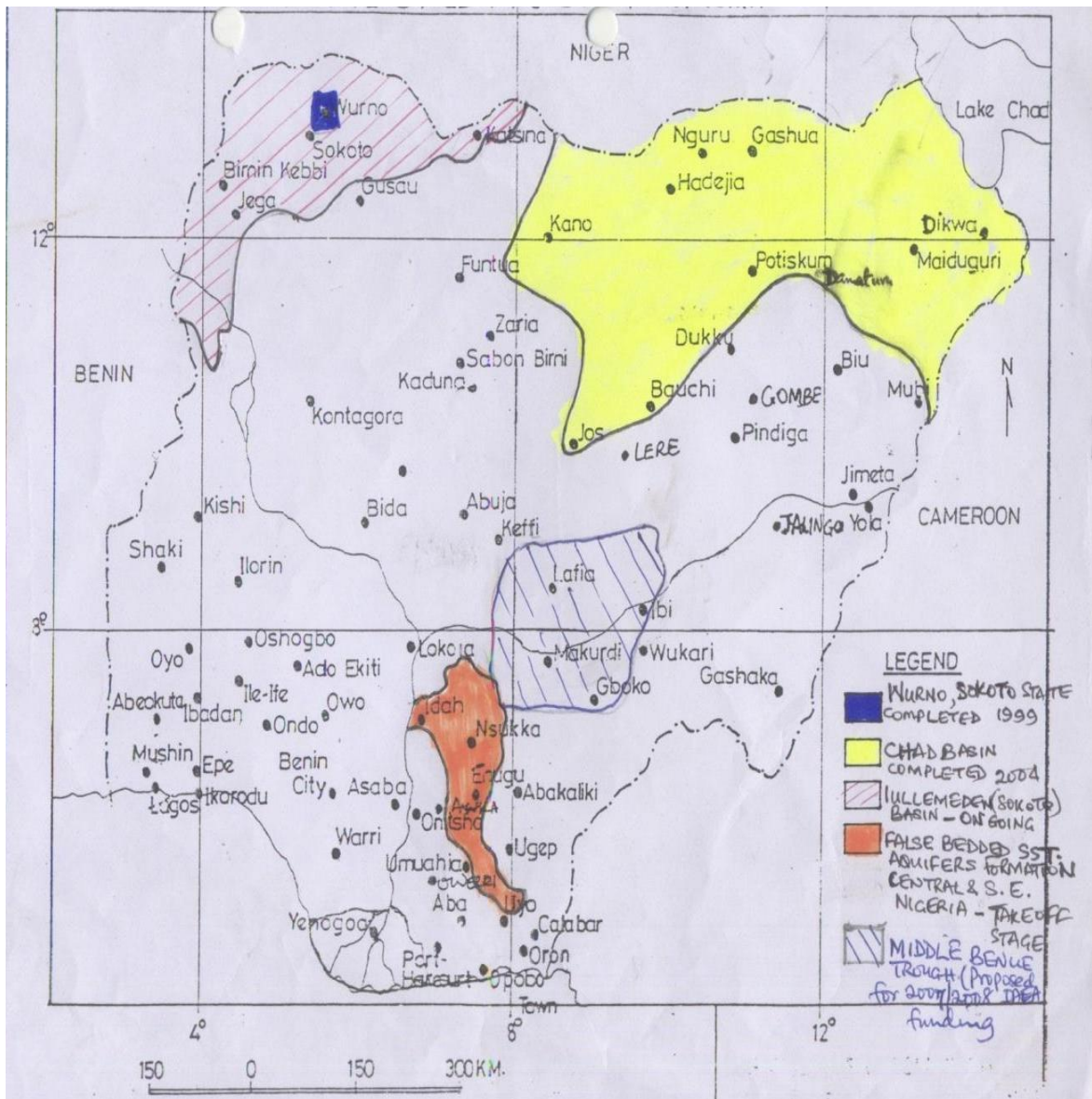


Figure 1.4: Location of isotope based projects in Nigeria (Source: NIHSA, 2012)

Hence, applications of isotope technique in conjunction with the hydro-chemical approach were utilized to assess the dynamics of water composition in Sokoto Basin. The results of the study would fill the data gap regarding water quality of the basin and contribute to improvements in the management of transboundary water resources.

1.4

Aim and Objectives

The main goal of this study is to apply isotope and hydro-chemical techniques to study the dynamics of water composition in Sokoto Basin. In order to achieve this goal, the following specific objectives are necessary:

- i. to determine the hydro-chemical composition and characterize the ground and surface water of the basin.
- ii. to determine the renewability of the aquifer; and inter-relationships between Aquifers of the basin.
- iii. to assess and evaluate the contaminant concentrations in the water systems and ascertain the usefulness of the waters for various purposes.

1.5

Scope of Study

The scope of this study is limited mainly to characterization, assessment and evaluation, of ground and surface waters in the Sokoto Basin, within Latitude of 12.13N to 13.36N and Longitude of 4.60E to 5.99E. This study excludes determination of the ground water evolution, sediment(soil) and atmospheric assessments.

1.6

Limitations of Study

One of the major limitations to the fieldwork in the study area is that availability of fund to drill wells to sample from as such data on the hydraulic head properties (such as the pressure head, elevation head and velocity head) of the aquifers were difficult to obtain. Monitoring boreholes do not exist, and monitoring of hydraulic heads in production boreholes was not possible, unless hand pumps or electric pumps are dismantled from the boreholes. This has not been realistic as part of this study, considering logistical problems, additional workload and the resistance from the local communities. Therefore, flow directions have been deduced

from digital elevation model of the basin using available borehole depths collected during field sampling exercise from Sokoto Basin authority in Sokoto State.

Furthermore, rainfall data and carbon isotope data were not collected during data collection due to logistic issues. However, Leibundgut *et al.*, (2009) suggested that in the event of limited rainfall data, data from the International Atomic Energy Agency (IAEA), Global Network of Isotopes in Precipitation (GNIP) can be retrieved and used for analysis with similar atmospheric circulation patterns. Onugba *et al* (1990), atlas of hydrology (IAEA, 2007); were referred to bridge the gap in precipitation data. Also, biological characteristics of the water quality were not assessed. It is therefore pertinent to note that these data could not militate against the realization of the goal of this study, but, their values were necessary to enrich the end product.

1.7 Description of Iullemeden Basin

Research needs to be placed in geographical and climatic features to make interpretation meaningful. This subsection focuses on geographical boundaries, topography, drainage, climate, vegetation, soil, geology, hydrology and hydrogeology.

The transboundary Iullemeden sedimentary basin according to (GEF, 2003) extends for approximately 1000 km from 10° N to 19° N, and for about 980 km from 1° E to 10° E with smaller fraction of the Iullemeden Formation located in Algeria in the north and in Benin which are not associated with the Iullemeden hydrogeological system. The sedimentary Iullemeden basin is described by features of major mountain ranges with the Air in the north, the Adrar in the North West and the Jos Plateau in Nigeria in the south (Kogbe, 1979 and GEF, 2003). The Iullemeden Basin is a multi-aquifer system that comprises of Cretaceous Continental Intercalaire sedimentary formations at the base and with overlying final Tertiary Continental Terminal regroupings. In the southeast, in the North-West Nigeria, the Iullemeden

Basin is locally referred to as Sokoto basin.

The Sokoto Basin, similar to Iullemeden Aquifer System consists of multi-aquifer system with Cretaceous Gundumi-Ilo at the bottom overlain by Rima Group, Sokoto Group and the Tertiary Gwandu aquifers. Although the Sokoto Basin of Nigeria appears extensive in area, it only represents about one-tenth of the entire Iullemeden Basin of West Africa (Greigert 1961; Adelana *et al.*, 2003). Prominent surface waters are the Rivers Rima and Sokoto, which confluence close to Sokoto town and drain into River Niger and ultimately into the Atlantic Ocean, (Anderson and Ogilbee, 1973). The landscape is characterized by the lithological differences between the rocks and lateritic iron stone (Kogbe, 1979); with undulating low relief of a maximum height of 240-340masl (Okuofu, 2006). Vegetation in the Sokoto Basin is that typical of the Sudan savannah. Soil profile in this region according to Kogbe (1979), shows a rather sandy topsoil and a clayey subsoil; but along the extensive fadama areas, the soil provides more fertile farm land; with an annual mean evapotranspiration which according to Sokona *et al.*, 2008 exceeds 2500 mm. The Sokoto Basin, like other basins in Nigeria has a two-season climate, dry and wet. In the wet season, (May to October), it is generally known that rains are induced by the northward movement of the moisture from Equatorial Maritime air mass from the Gulf of Guinea, whose prevailing winds are from the southwest. The average monthly precipitation ranges from 2.99mm (February), to 188.38mm (August), (AzTech, 2010); and in the dry months from October through April, the dry dust-laden harmattan winds of the Tropical Continental mass, blow in from the northeast. The coolest months in the Sokoto region are December and January when the average daily minimum temperature declines to 17.5°C. The hottest month varies between April and May with average temperature of about 26.4°C (AzTech, 2010). The low relative humidity in the area has been observed to coincide with months of low rainfall.

Two major ethnic groups inhabit the area, the Fulani and the Hausa. The population density is such that the high concentrations of people are in cities and towns in the States of Sokoto, Kebbi and Zamfara with a population of approximately six million and close to four million in the Iullemeden Basin, (Sokona *et al.*, 2008). The most important environmental factor influencing the population is the availability of potable water in the dry season, (Oteze, 1991)The basin covers a zone that has been affected by drought in the last several years and has witnessed a strong exploitation of the groundwater resources. The low-lying flood plains (*fadama*) are used during the dry season for irrigated agriculture, Okuofu (2006). The economy of the province depends chiefly on agriculture; grains, rice, cotton, tobacco, and groundnuts (peanuts) are the most important crops. Fishing from the major river of the region attracts tourists annually especially during the Argungu fishing festival. Also, more than 100,000 cattle are exported annually to other regions of Nigeria. So, livestock rearing and other agricultural activities exist. The processing of hides and skins, tannery, textile manufacture, local aluminium utensil production and acement factoryare among the growing industries in the region.

1.7.1 Hydrology of the Study Area

The main drainage axes of the Continental Terminal (TC) water table in Iullemeden Aquifer System (IAS), is oriented northwest- southeast and northeast-southwest, (Fig.1.5). The main recharge segments of IC are the Hoggar Mountains in the north and the Rima River in the south, with the groundwater flow mainly from the northwest, north and northeast towards the south (OSS, 2008).

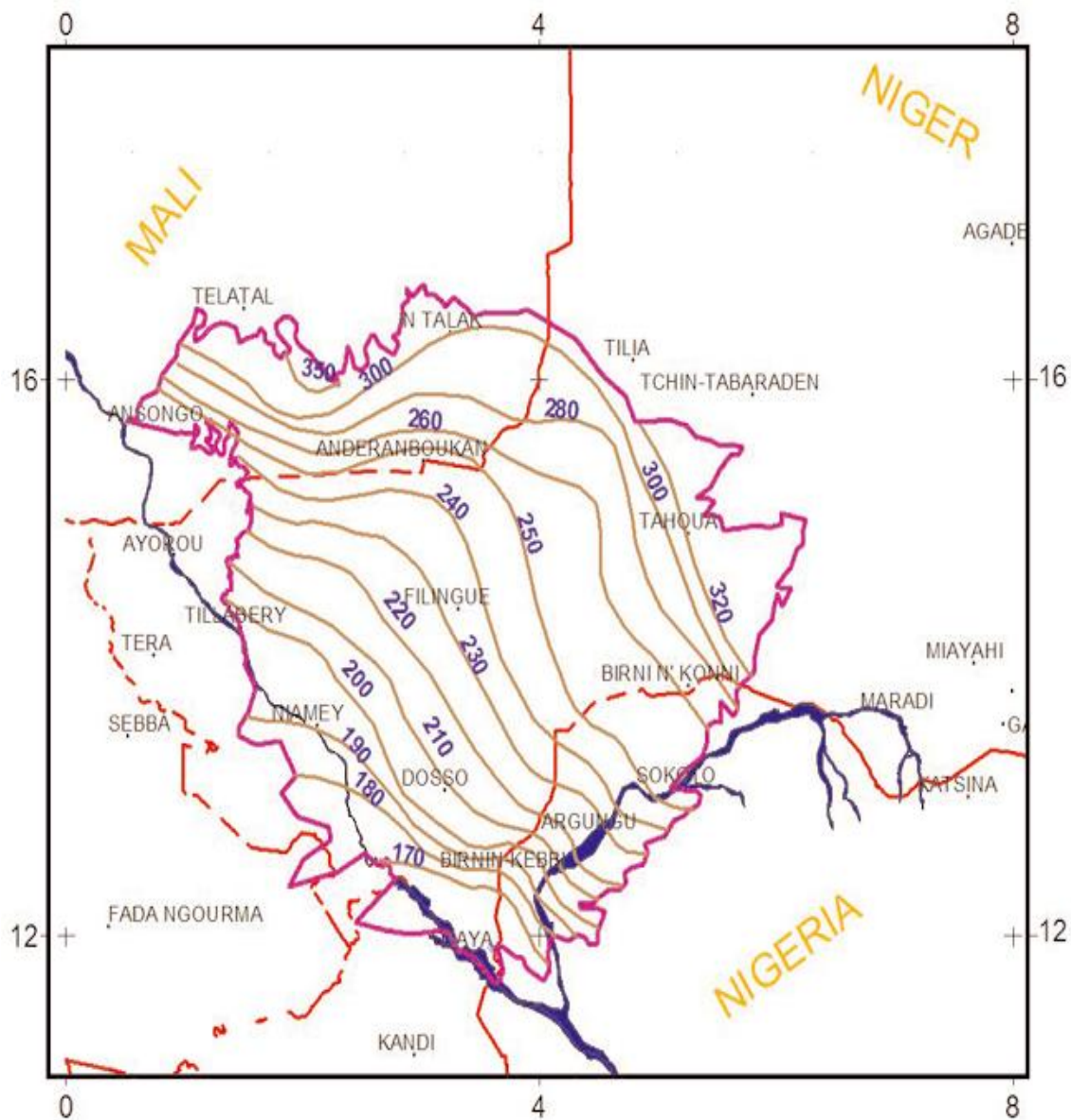


Figure 1.5: Piezometric map of TC Aquifer, (OSS, 2008)

The Niger River is the main drainage network (Sokona *et al*, 2008); while Rima River is the drainage zone also one of its tributaries (OSS, 2008). Sokoto and Rima River is the main drainage network in the Sokoto Basin, (Anderson and Ogilbee, 1973). The principal water-bearing beds in the Sokoto sediments are the surface laterites, sandstones and grits in the Gwandu Formation; limestone beds in the Kalambaina Formation; sandstones in the Wurno and Taloka Formations as well as grits and sandstones in the Gundumi-Ilo Formations (Jones, 1948; Anderson and Ogilbee, 1973; Kogbe, 1979). The headwaters of the Rivers Sokoto

and Rima and their tributaries originate in pre-Cretaceous crystalline rock terrain east of the Sokoto Basin and flow west and south across a terrain underlain by sedimentary rocks of the Gundumi-Ilo Formation, the Rima and Sokoto Groups, and the Gwandu Formation, (Anderson and Ogilbee, 1973). There are other principal tributaries to the main drainage networks such as Shella river, Gulbin Ka, Bunsuru river, Gagere river, Kware river, Zamfara river among others (WARDROP, 1986) (Fig. 1.6).

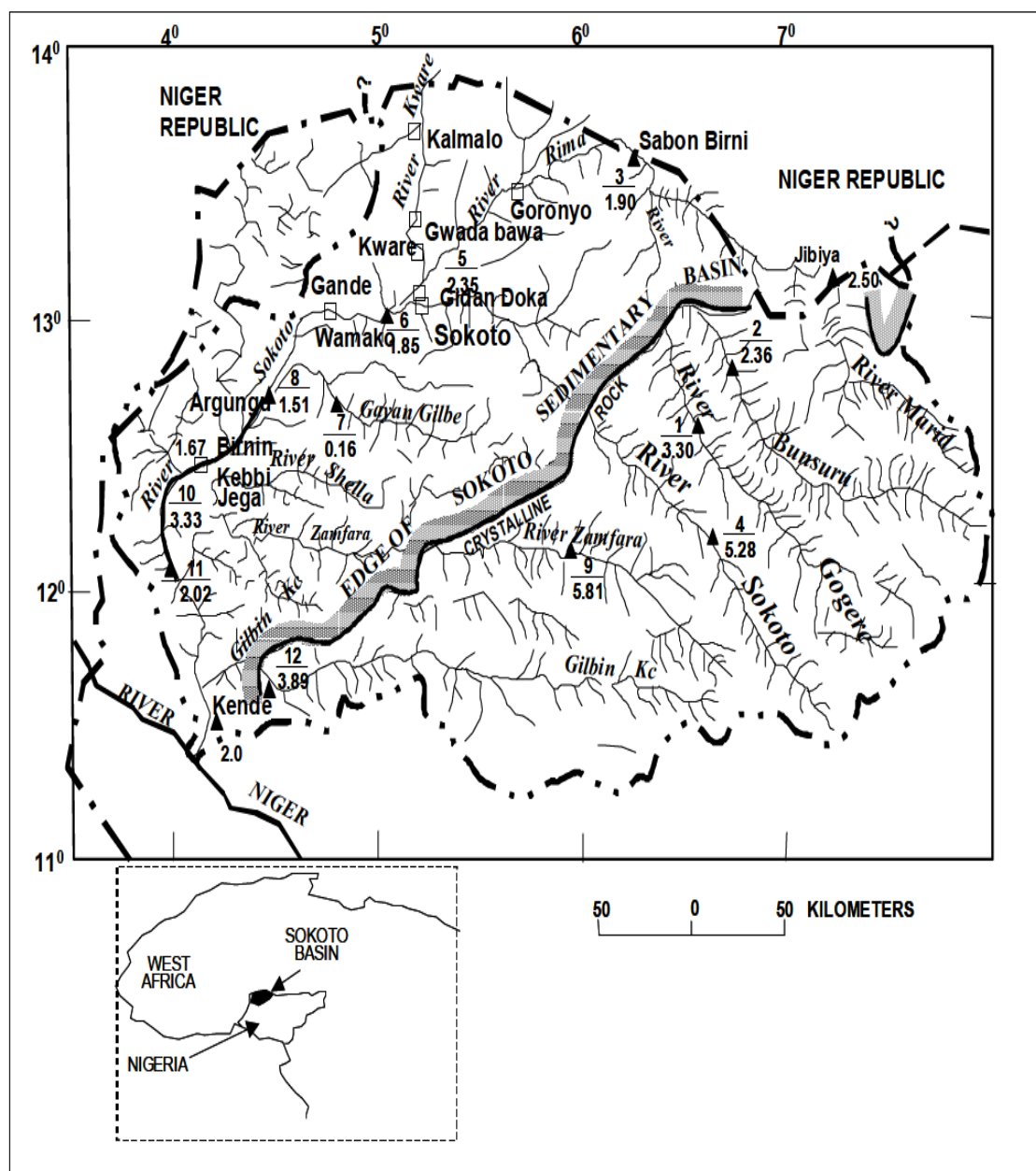


Figure 1.6: Tributaries Pattern of Sokoto Basin (Anderson and Ogilbee, 1973)

Rainfall in this area percolates directly into the sandy soil, or flows in minor tributaries where it infiltrates or evaporates; and may eventually dry out during the peak of the dry season. Water resources can be divided into precipitation, surface water and groundwater.

1.7.2 Hydro-geology of the Study Area

The hydrogeological setting is essentially Continental Intercalaire and Continental Terminal of the Iullemeden Basin. Sokoto Basin, which constitutes the Nigerian sector of the Iullemeden sedimentary basin, is underlain by a sequence of interbedded semiconsolidated gravel, sand, clay, and limestone, (Anderson and Ogilbee, 1973). The sediments of the Iullemeden Basin were deposited during three main phases: Continental, Mesozoic and Tertiary with an intervening marine Maastrichtian to Paleocene phase, (Kogbe, 1979). The succession of sediments in Sokoto basin (after Adelana *et al.*, 2003) is presented in Table 1.1 for better understanding of the geology of the area.

Table 1.1: Summary of Lithological Sequence in Sokoto Basin, (Adelana, *et al* 2006)

AGE	GROUP	ENVIRONMENT	FORMATION	HYDROLOGICAL SIGNIFICANCE
Quaternary		Continental	Sandy drifts, laterites	Aquiferous
Eocene-Miocene	“Continental Terminal	Continental	Gwandu. F	Prolific Aquifer
UpperPaleocene	Sokoto Group	Marine	Gambia. F Kalambaina. F Dange Formation	Aquiclude Aquifer in outcrop Area Aquiclude
Maastrichtian	Rima Group	Brackish water with brief Dukamaje marine Intercalation	Wurno Formation Dukamaje Formation Taloka Formation	Moderate Aquifer Aquiclude Good Aquifer
Turonian	“Continental Intercalaire”	Continental	Gundumi-Ilo. F	Moderate Aquifer Locally flowing
Precambrian			Basement Complex	Isolated Aquifers But mostly aquiclude

F = Formation

Overlying the Pre-Cambrian basement unconformably is the oldest rocks of the sedimentary basin whose sequence is tertiary deposits of the Gundumi-Ilo Formation of Cretaceous age, (Anderson and Ogilbee, 1973). It consists of principal heavy minerals of Opaques: *Zircon*, *Tourmaline*, *Sillimanite*, *Garnet*, *Kyanite*, *Epidote* and *Chlorite* (Kogbe, 1979). Also, it contains comparatively coarser materials than any of the younger overlying formations of the Sokoto Basin. The features like sand and gravels are composed chiefly of angular to sub-angular quartz grains, of beds rich in feldspathic and micaceous material. The heavy

minerals assemblage according to (Kogbe, 1979), are of high grade metamorphic rock components (like gneisses and schists) and acidic igneous rocks.

Above the Gundumi – Illo Formation lies the Cretaceous Rima Group (Wurno, Dukamaje and Taloka Formations). The Rima Group consists of sequence of fine gray sand, clay deposits and marly limestone and shale (Anderson and Ogilbee, 1973). The heavy mineral content reported by Kogbe, (1979) is predominant Opaque minerals of *Kyanite, Tourmaline, Zircon, Staurolite and Hornblende* which are of Igneous and Metamorphic rock origin. Parker *et al.*, (1964) noted that the Rima Group consists of white fine-grained friable sandstones containing some thin intercalated beds of Carbonaceous mudstone or shale (Taloka and Wurno Formations), that are separated by the fossiliferous shaly Dukamaje Formation. According to Anderson and Ogilbee (1973) the Dukamaje Formation consists of thin limestone, mudstone and some gypsum. The dominant clay minerals in Maastrichtian marine to brackish water Formations in northwestern Nigeria are Chlorite Illite, and gypsum, usually formed in an alkaline reducing environment (Kogbe, 1979).

Overlying the Maastrichtian age is the Paleocene age of the basin. The Paleocene Dange and Gamba Formations, (mainly shales), are separated by the calcareous Kalambaina Formation, (Kogbe, 1979, Adelana *et al.*, 2003). The upper part contains phosphatic nodules and gypsum, while the lower part is calcareous with occasional limestone bands. Overlying the Maastrichtian unconformably is the Eocene to Miocene aged Formations.

The overlying continental Gwandu Formation (Continental Terminal), is of Tertiary age, (Jones, 1948; Kogbe, 1989)(Fig.1.7). The sand beds are fine to very coarse, predominantly quartz, containing some limonite nodules, cemented in places by limonite. Kaolinite is the dominant clay mineral in continental Gwandu Formation.

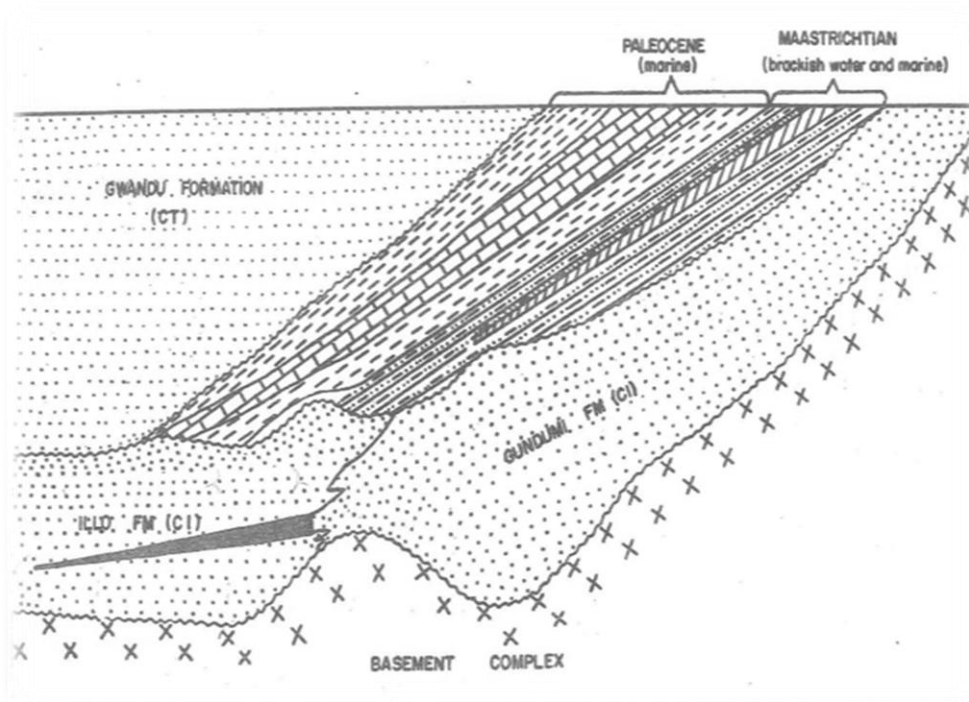


Figure 1.7: Geological section of Sokoto Basin (Source: Kogbe , 1979)

Illite, Chlorite and Kaolinite were derived from the weathering products of the metamorphosed basement rocks. Kaolinite is formed mainly from the weathering of Micas and Feldspars.

CHAPTER TWO

2.0 LITERATURE REVIEW

Application of isotope hydrology techniques to determine the interplay of recharge from rainfall, irrigation return flows and contribution to annual flooding to groundwater as well as quantification of water quality changes in the aquifer systems was actualized in the study of Wurno Irrigation scheme area and environment between 1997 to 1999 by Hanidu and team under Nigeria Hydrological Services Agency (NIHSA), in an IAEA model project RAF/8/022 following the intensive groundwater abstraction from the shallow aquifers of the “fadamas” for accelerated irrigation activities under the World Bank-assisted National Fadama Development Project (NFDP) which commenced in the area in 1993.

Between 2004 and 2008, Nigeria participated in Project RAF/8/038 alongside Niger and Mali, to define water quality problems. However, in the project, it is vital to note that no isotope data were acquired (NIHSA, 2012). But, Alagbe (2004) applied the isotope and hydrogeological technique to study Kalambaina Formation; Adelana *et al.*, (2003) and (2006) applied similar approach to characterize waters from the Wurno Formation.

It is in this respect, that the present study is structured to fill the vacuum in water quality data, for improving trans-boundary management of water resources. Through, application of Isotope and hydro-chemical techniques to study the dynamics of water compositions of the Sokoto Basin in collaboration with Nigeria Hydrological Services Agency (NIHSA).

2.1

Environmental Isotope

The term isotope was used by Soddy (1913) to describe nuclides which occupy the same position in the periodic table but which differ in their nuclear properties. The name Isotope was coined from Greek words *isos* meaning equal and *topos* representing place and reflect the fact that isotopes are at the same place on the periodic table stated (Aelion *et al.*, 2010). The notion of environmental isotopes has been used by several authors (Fritz and Fontes, 1980; Clark and Fritz, 1997; Kendall and Mc Donnell, 1998; Cook and Herczeg, 1999; Mook and De Vries, 2000; Johnson, 2004, Flanagan *et al.*, 2005; Hoefs, 2009; Leibundgut *et al.*, 2009; Aeloin *et al.*, 2010; Singhal and Gupta, 2010; Kebede, 2012; Yidana, 2013) as a tracer in hydrology. Aelion *et al.* (2010) stated that environmental isotope have no exact definition, as such, that environmental isotopes do not imply that the isotopes were inherently produced. Leibundgut *et al.* (2010), in support of Aelion's statement used ^{14}C as an example of an isotope that is of natural reaction and anthropogenic origin.

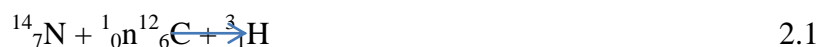
The most common environmental Isotopes are the isotopes of water molecules or isotopes of hydrogen and oxygen (Mazor, 2004; Singhal and Gupta, 2010). The isotopes of water molecules may be divided into light ($^1\text{H}_2^{16}\text{O}$) and heavy ($^1\text{HD}^{16}\text{O}$ and $^1\text{H}_2^{18}\text{O}$) water molecules (Mazor, 2004; Kumar, 2010; Kebede *et al.*, 2010; Kebede, 2012). Molecules containing heavier isotopes move and vibrate slower than their light-isotope counterparts. As such, when water evaporates, the vapor-phase water is enriched in the light isotopes ^1H and ^{16}O while the remaining liquid phase is enriched in the heavy isotopes ($^1\text{H}_1$, $^3\text{H}_1$, ^{17}O and ^{18}O) (Fitts, 2002). Isotopes of hydrogen and oxygen being an integral part of water molecule and an environmental tracer, it can trace the history of water, transport processes in aquifers, interactions and mixing and applied in recharge estimation (IAEA, 1983, 1989; Clark and

Fritz, 1997; Kehew, 2001 and Aggarwal *et al.*, 2005). According to (Kumar, 2010), Isotope may be radioactive(also called unstable) or stable.

2.2 Radioisotopes

Radioisotopes describes isotopes produced naturally by the cosmic ray interaction with atmosphere and isotopes introduced into the environment through testing of nuclear weapons and atomic installations, (Singhal and Gupta, 2010).

L'Annunziata (2007), defined cosmic radiation as the background radiation (are charged particles and nuclei with lifetimes of 10^6 years or longer originating from space that strike the top of the atmosphere from all directions) which contributes to the interference in the measurement of the levels of radioactivity in soil, plants and waters. The phenomenon of disintegration of unstable atoms to the stable form is known as radioactivity (Kumar, 2010). Unstable nuclides are radioactive isotopes. The nuclei of radioactive isotopes spontaneously disintegrate ejecting high energy radiation (in the common forms of alpha particles, beta particles, neutrons and gamma rays) in the process (Fitts, 2002; Dickin, 2005). Tritium (^3H or T) is a radioactive isotope of hydrogen, and perfect water tracer because it is incorporated directly into water molecules. It originates from nuclear reaction between atmospheric nitrogen and thermal neutrons (see equ.2.1) and enters the hydrologic cycle after oxidation to $^3\text{H}^3\text{HO}$ (see equ.2.2), thereafter, emits low energy beta particles ($E_{\text{beta}_{\text{max}}} = 0.0816\text{MeV}$) with half life of 12.3 years that makes it useful for short term age dating (Libby, 1961; Unerweger *et al.*, 1980; Clark and Fritz, 1997; Fitts, 2002; Longmire *et al.*, 2007; Moses and Bernd, 2008 among many other).



Where superscripts represent the atomic mass and subscripts represent the atomic number of each isotope.

Pre-1950s, tritium has been present in the atmosphere at low levels due to cosmic radiation. In that respect, (Kaufman and Libby, 1954) estimation of level of tritium concentration in precipitation range from 3 to 7 TU. As such, (Roether, 1967) noted that under undisturbed natural conditions the T concentration in precipitation is probably about 5TU. Also, (Andrews *et al.*, 1987) recorded low concentration of tritium (less than 0.01TU) in groundwater. Post-1950s to 1970s, tritium production is by anthropogenic processes from: nuclear weapons production and testing, nuclear power fuel cycle resulting in environmental pollution (Fitts, 2002; Mazor, 2004; Longmire *et al.*, 2007; Moses and Bernd, 2008; and Kumar, 2010).

Generally, the radiation and the decay per unit time are measured using counting device such as the Geiger counter, Semiconductor counter and Scintillation counter (Dickin, 2005). Tritium is measured with a liquid scintillation (LS) counter. The results of sample laboratory analysis may be reported in Tritium Unit (TU), Becquerel (Bq), Curie (Ci) or disintegrations per second per unit mass or volume of water (Dickin, 2005; Moses and Bernd, 2008 and Kumar, 2010). The Energy of disintegration or radiation is denoted by KeV or MeV (Kumar, 2010). Tritium Unit (TU) is still widely used for various hydrological studies. There are other varieties of artificially produced radioisotopes like ^{60}Co , ^{82}Br , ^{131}I , ^{137}Cs , ^{198}Au , among many others that are used for various hydrological investigations.

2.3

Stable Isotopes

The most common stable isotopes used in water studies are the stable isotopes of water molecules (Leibundgut, *et al.*, 2009), ^2H and ^{18}O . Among the stable isotopes, Singhal and Gupta (2010) stated ^2H and ^{18}O are used for determining the source of water and its genesis (like mixing of waters of different origin, salinization processes among others) while ^{13}C , ^{15}N and ^{34}S are used in pollution studies. Advances in mass spectrometry and with the advent of TIMS-techniques and the introduction of multiple sample collector like Inductively Coupled Plasma Mass Spectrometry, ICP-MS, Tunable Diode Laser Spectrograph, TDLAS, environmental isotope methods of determination have shifted towards smaller sample amounts and the compound specific analysis of isotopes (Hoefs, 2004; Leibundgut, *et al.*, 2009; Aelion *et al.*, 2010).

Stable isotope values are usually reported in the delta (δ) notation, a value expressed in parts per thousand (‰, per mil) (Aelion *et al.*, 2010). The laboratory results of ICP-MS analyses are usually reported as a deviation from the isotopic ratio because it leads to greater analytical accuracy, (Fitts, 2002; Mazor, 2004; Hiscock, 2005; Aelion, 2010).

Isotope ratio (R) are measured for samples and standard by mass spectrometry and the relative measure delta (δ) is calculated as written below for the ^{18}O and ^{16}O (Coplen, 1996).

$$\delta^{18}\text{O} = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}} \times 1000 \quad 2.3$$

With R_{sample} being the $^{18}\text{O}/^{16}\text{O}$ ratio determined by mass spectrometry and R_{standard} being the abundance ratio of the international standard (Aelion *et al.*, 2010).

According to (Hiscock, 2005), the accepted international standard for isotopes of water molecules is V-SMOW (an acronym for Vienna Standard Mean Ocean Water) with values of

$\delta^{18}\text{O}$ and $\delta^2\text{H}$ equal to zero and also VPDB-belmenide fossil from Pee Dee Limestone formation in USA or pmc (percent modern carbon) standard for some other isotopes like isotopes of carbon.

In δ (delta)notation, positive values indicate an enrichment of ^{18}O or ^2H compared with the standard being used; whereas negative values signify a depletion of heavier isotopes in the sample, (Mazor, 2004; Kumar, 2010; Kebede, 2012; and Yidana, 2013) Plot of $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ usually form a linear trend called the Global Meteoric Water Line (GMWL), a concept useful in interpretation of stable isotopes results (Craig 1961a and 1961b; Dagassard, 1964; Gordon *et al.*, 1992; Fitts, 2002; Mazor, 2004; Hoefs, 2009; Kebede, 2012).

2.4 Global Meteoric Water Line

The meteoric water line is a reference line for the understanding and better interpretation of local groundwater type, origin and movement (Mazor, 2004). The best linear relation between δD and $\delta^{18}\text{O}$ can be written in a standard form of equation for straight line as:

$$\delta\text{D}\text{‰} = A\delta^{18}\text{O} + d, \quad 2.4$$

where A is the slope and d is the intercept of δD vs. $\delta^{18}\text{O}$ line of fresh global meteoric waters, Kumar (2010). The deviation in groundwater isotope compositions from the meteoric water line can be used to estimate average recharge rates in arid settings and also as tracers to characterize groundwaters from different sources (Allison *et al.*, 1983).

Contributing to the establishment of Global Meteoric Water Line (GMWL), Northern hemisphere reference line using the existing good linear relationship between the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of precipitation from various parts of the world as early as in the 1960s includes Craig, 1961b and Gordon, *et al.*, (1992) and Dansgaard (1964). The plot of these isotopes on a

composite graph fall on a line defined by the following equation called the Global Meteoric Water Line (GMWL) or Craig Line:

$$\delta^2\text{H} = 8\delta^{18}\text{O} + 10 \quad 2.5$$

Depending on the humidity and temperature conditions locally the $\delta^{18}\text{O}$ - $\delta^2\text{H}$ plot of local rains may deviate from the GMWL and form a local meteoric water line (LMWL) see (Fig 2.1).

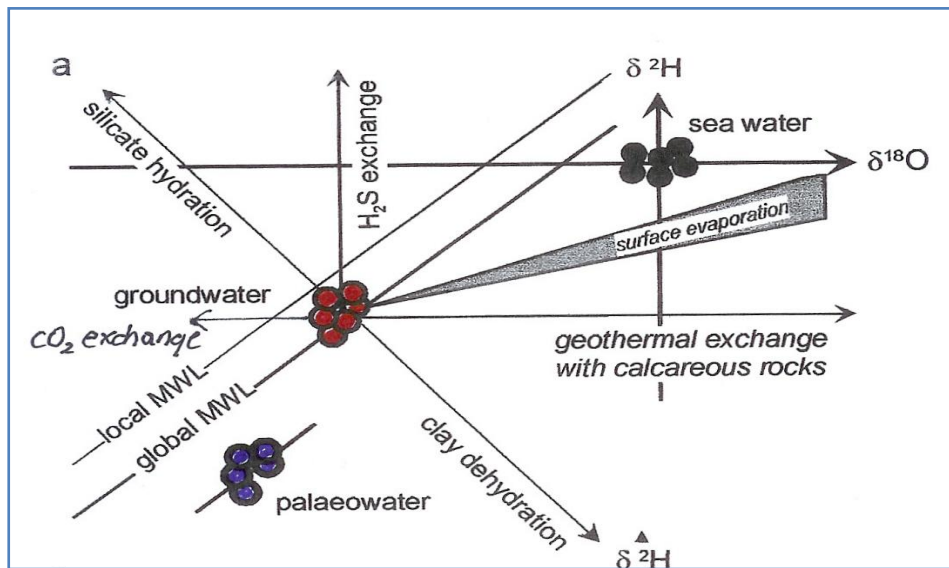


Figure 2.1: Isotope conventional standard graph for isotope interpretation (Kebede, 2012)

The Figure 2.1, according to (Kebede, 2012) reflects processes that modify the initial isotopic composition of given meteoric water in the environment. The global meteoric water line is the reference against which comparison can be made to understand isotope effects that have taken place, in order to understand the processes of recharge, evaporation and mixing, (Kebede, 2012). Hoefs (2009) defined the effects as the differences in chemical and physical properties arising from variations in atomic mass of an element.

2.5

Isotope Effects

The Isotope effects from Kebede (2012) perspective are associated with the processes of depletion or enrichment of heavy isotopes in a given hydrologic compartment and have wider implication in hydrological studies. The variation of isotopic composition in environment (either in water, sediments or atmosphere) is governed by various factors (also known as isotope effects) like, altitude, latitude, evaporation, temperature, paleoclimate, amount of rain, etc, (Mazor, 2004; Leibundgut *et al.*, 2009, Kumar, 2010; Kebede, 2012)

2.5.1 Altitude effect

The precipitation is depleted in heavy isotope composition as temperature decreases at higher altitude (Leibundgut *et al.*, 2009; Kumar, 2010; Kebede, 2012). This effect can be used to validate origin of water and recharge altitude. The corresponding altitude isotope equations after (Payne and Yurtsever, 1974) are: $h = -320\delta^{18}\text{O} - 2564$ and $h = -40.2\delta\text{D} - 2052$, where h is the altitude in meter above sea level (masl) (Mazor, 2004).

2.5.2 Latitude effect

Similar to altitude effect, as latitude increases, the temperature decreases. Thus, the water vapors deplete in heavier isotopes with the increase in latitude (Dansgaard, 1964; Yurtsever and Gat, 1981; Mazor, 2004; Kumar, 2010; Kebede, 2012).

2.5.3

Evaporation effect

This effect results from two prominent features. Typical example of the features includes evaporation of rainfall while the rain is making their way to the ground and evaporation of waters exposed to vapor loss (such as lakes, wetlands waters, running waters, reservoirs and oceans). Residual waters that have undergone evaporation plot along a local evaporation line see (Fig.2.1). Enrichment of rainwater and deviation from the global meteoric water line tend

to result in arid and semi-arid environment due to intensive evaporation of rain droplets in dry atmosphere (Mazor, 2004).

2.5.4 Paleoclimate effect

This effect is one of the vital tools in identifying paleoground water. Late Pleistocene paleogroundwaters from temperate regions will be isotopically depleted with respect to modern waters and shifted along the GMWL towards negative values as shown in (Fig. 2.1).

The more theory of isotope effects and fractionation mechanism are documented in detail in the works of these authors Biegleisen and Meyer (1947); Urey (1947); Melander (1960); Bigeleisen (1965); Richet *et al.*,(1977); O'Neil (1986); Criss (1999); Chacko *et al.*,(2001); Schauble (2004).

2.6 Isotope fractionation

The partitioning of isotopes between two substances or two phases of the same substance with different isotope ratios is called isotope fractionation, (Hoefs, 2009).Phase changes, evaporation, condensation, freezing, sublimation, melting and somechemical reactions are associated with an isotopic fractionation (Kebede, 2012). Isotopically light water molecules evaporate more efficiently than the heavy ones. As a result, an isotopic fractionation occurs at partial evaporation of water: the vapor is enriched in light water molecules, reflected in relatively negative δD and $\delta^{18}O$ values, (Mazor, 2004). In contrast, the residual water phase becomes relativelyenriched in the heavy isotopes, reflected in more positive δD and $\delta^{18}O$ values.

2.7 Causes of Change in Water Quality

Increased industrialization, urbanization and agricultural activities have degraded the quality of water in developing and developed countries. Water contamination source can be classified

into geogenic (natural) and anthropogenic sources, (Singhal and Gupta, 2010). The term contamination is used for addition of any solute into the hydrological system as a result of man's activity while the term pollution is restricted to a situation when the contamination attains levels that are considered to be objectionable (Freeze and Cherry, 1979). Illustrated in Fig (2.2) are some of the groundwater contaminants origins. There could also be deterioration in water quality due to natural reasons namely dissolution of rock material, and degradation due to chemical reactions (like ion exchange, membrane filtration and sulphate reduction) within the aquifer matrix (Grutzmacher, 2013).

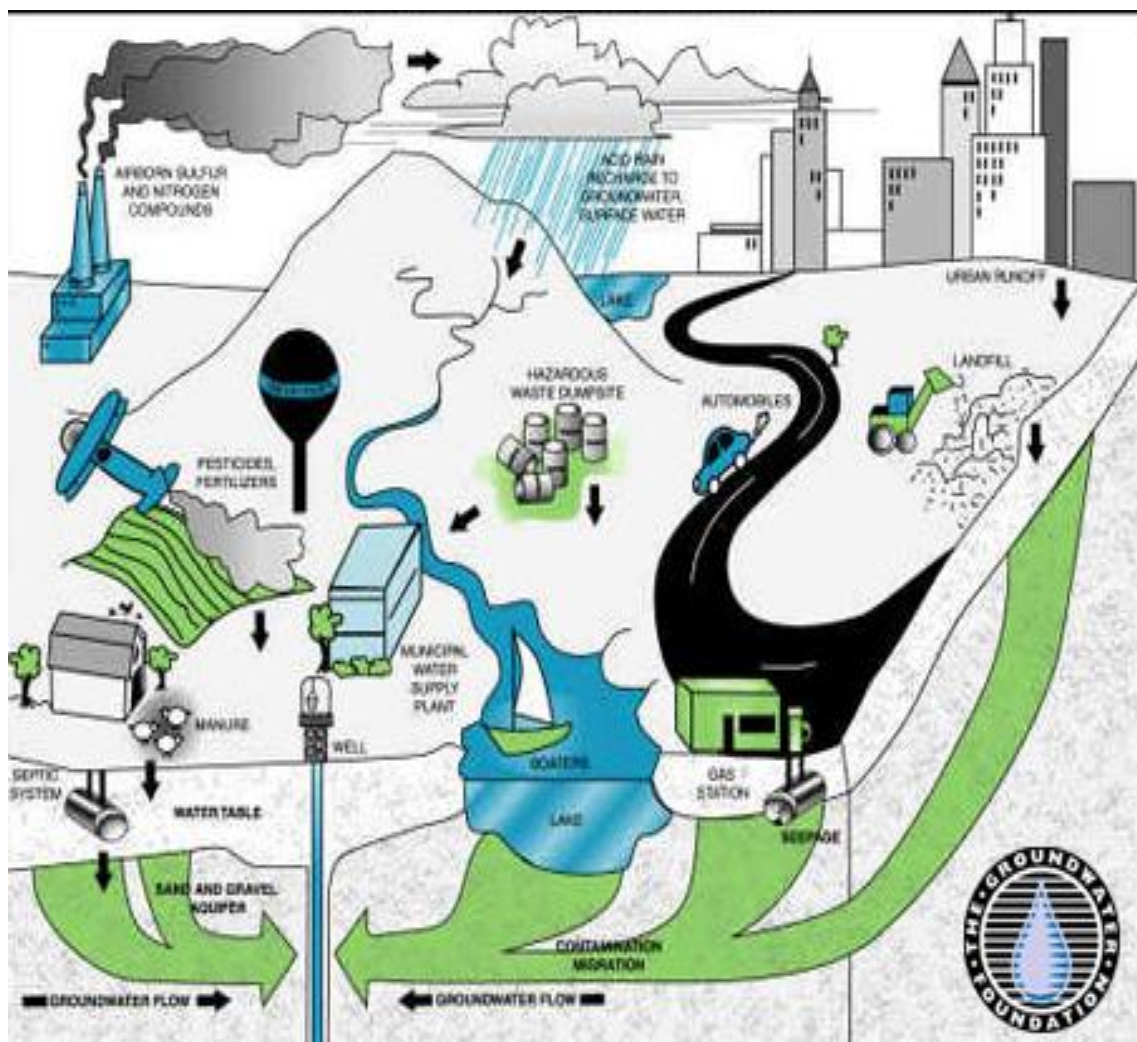


Figure 2.2: Sources of water contaminants (Source: Groundwater Foundation, 2000)

2.7.1 Geogenic sources

Geogenic source of water contamination involves natural processes leading to the concentration of certain toxic materials or substances beyond acceptable limits for human consumption like dissolution of aquifer materials. Increased concentration of fluoride, chloride, arsenic, iron and other heavy metals in groundwater is attributed to this type of contamination (Singhal and Gupta, 2010). The common forms of geogenic contamination with human health impacts includes increase concentrations of arsenic and fluoride (Johnson *et al.* 2008), elevated concentration of uranium (Smedley *et al.*, 2006; Stalder *et al.*, 2012), and chloride (Panno *et al.*, 2006).

2.7.2 Anthropogenic sources

These include man made contributing factors to water deterioration such as:

i. Industrial Activities

Contributing to sources of pollution in the urban environment include highway runoff potentially directed to soakaways (Price *et al.*, 1989), salt and urea used in de-icing roads, paths and airport runways (Howard and Beck 1993), application of pesticides in park and gardens among others. The waste water discharged from industries carries with it a variety of dissolved and suspended impurities, the composition (which could be either inorganic or organic contaminants) of which depends on the type of industries and the processes used. For example, the dewatering of former open pit lignite mines in Lusatia (Germany) lead to aeration of aquifers and subsequent pyrite oxidation, a process which increases Fe and SO_4 concentration whilst reducing pH (Hiscock, 2005).

Groundwater contamination from industrial wastes usually begins with the practice of disposing of untreated industrial chemical wastes in surface impoundments like unlined landfills or lagoons. Effluents discharged without proper treatment cause contamination of surface water and groundwater. For example, high concentrations of Cr, Ni, Cd, Pb and Zn in

surface water and groundwater are reported from several places due to industrial activities globally (Europe, Asia and Africa) (Kakar 1988; 1990; Handa 1994, Agalaba *et al.*, 2011, Guilherme *et al.*,2011, Likuku *et al.*, 2013 and others). As industrial waste represents a significant source of groundwater contamination, water practitioners expend an increasing amount of time in abating or mitigating pollution events that damage groundwater supplies.

ii. Municipal landfill Waste

The landfilling of municipal waste is common practice, with older sites (like abandoned quarries, abandoned pit toilet, refuse dumps or natural depression like gully erosion sites) up until the late 1980s (Singhal and Gupta, 2010) formerly operated under a ‘dilute and disperse’ principle where leachate generated in the waste was allowed to migrate away from the site and disperse in groundwater below the water table. The leachate from landfills or dumpsite may contain large number of contaminants that can cause severe deterioration to groundwater quality (Fig.2.3).



Figure 2.3: Waste disposal sites as contaminants input in water bodies

Municipal landfill leachate are highly concentrated complex effluents which contain dissolved organic matters; inorganic compounds, such as ammonium, calcium, magnesium, sodium, potassium, iron, sulphates, chlorides and heavy metals such as cadmium, arsenic, chromium, copper, lead, nickel, zinc; and xenobiotic organic substances (Lee, *et al.*, 1986; Lee and Jones, 1993; Christensen *et al.*, 2001; Stollenwerk and Coleman, 2003; Tengrui *et al.*, 2007; Ogundiran and Afolabi, 2008). Besides, landfill leachate has high levels of BOD, COD, ammonia, chloride, sodium, potassium, hardness and boron (Longe and Enekwechi, 2007). Also, Lee and Jones (1993) described typical composition of municipal landfill leachate. The chemical composition of the leachate varies due to a number of different factors such as age, type of waste, operational practices at the site and percolation rate through the fill to the groundwater. From various studies, over 40 organic compounds had been identified in leachate contaminated groundwater. Wood and Curran (1998) reported an average arsenic concentration in leachate contaminated groundwater as high as 21 µg/L. In the U.S., Fitts (2002) stated that older dumps, numbering in the tens of thousands have generated many leachate plumes which have reached kilometers in length in more permeable settings. One of the more common measures taken to avoid groundwater contamination is to locate landfills in areas composed of rock or soil of low permeability so that water does not percolate through the landfill into the underlying aquifer. Dolk (1999) reported that aquifers should be located within 7km radius to a landfill to avoid possible contamination of groundwater. Moreso, modern landfills have low-permeability caps to limit infiltration of leachate, liner and leachate collection systems to intercept and treat leachate constituents generated (Fitts, 2002).

iii. Agricultural Activities

These are also important contaminant sources which cause contamination of groundwater due to greater use of fertilizers (inorganic fertilizers and organic manure), pesticides for obtaining

higher crop yields (Hiscock, 2005; Singhal and Gupta, 2010) and human and animal waste excreta. These contaminants can leach to water-bearing aquifers below ground from applications onto crop fields, seepage of contaminated surface water, accidental spills and leaks, improper disposal, and even through injection of waste material into wells (Spellman, 2008). The inorganic fertilizers constitute nitrogen, phosphorous and potassium. Nitrogen, in the form of NO_3^- , is more soluble in groundwater as compared with phosphorous while K^+ has low mobility due to cation exchange. High amount of NO_3^- in groundwater can also be due to contamination from human and animal waste excreta. The health effects of high nitrate concentrations in excess of European and WHO water quality standards (50 mgL^{-1}) are concerned with methaemoglobinaemia ('blue baby' syndrome) in infants (Walton 1951; Craun *et al.* 1981) and gastric cancer (National Academy of Sciences 1981; Nomura 1996). Environmental impacts associated with excessive nitrate in the aquatic environment are eutrophication of inland and coastal waters and the consequent loss of biodiversity (Hecky and Kilham 1988; European Environment Agency, 2003). Nitrate concentration of groundwater due to the use of synthetic and organic fertilizers poses serious problems in USA especially in areas where corn and wheat are grown (Singhal and Gupta, 2010). In Jaffna Peninsula of Sri Lanka, groundwater in Miocene limestones contains in excess of 90 mgL^{-1} of NO_3^- , which is mainly due to the increased use of inorganic fertilizers (Skinner, 1985). Higher concentration of NO_3^- ($>100 \text{ mgL}^{-1}$) is also reported from groundwater in the shallow unconfined aquifers of the semi-arid regions of western parts of India. The contamination of groundwater by phosphorous is less than nitrogen, as PO_4^{3-} is easily adsorbed on sediments (soil) and has low mobility in groundwater. However, surface water may have comparatively higher amount of phosphorous which causes excessive vegetative growth in lakes and reservoirs (Schwartz and Zhang, 2003).

Pesticides refer to the group of synthetic organic chemicals used mainly as fungicides, herbicides and insecticides (Hiscock, 2005). The use of pesticides is rapid in many developing countries compared to the developed world (Singhal and Gupta, 2010). In India, the average rate of application of pesticides to agricultural land is about 180 grams per ha (Handa, 1994). Canter *et al.* (1987) have given a good account of the effect of pesticides on groundwater quality, based on field, laboratory and model studies. The contamination of groundwater by pesticides is dependent on the properties of the soil, and application factors. The chance for pesticide contamination is higher in surface water than groundwater due to the adsorption of pesticides by clay mineral grains and organic matter degradation by bacteria. Some pesticides with higher solubility in water have significant mobility in some type of aquifer materials, such as clean sands and gravels (Freeze and Cherry, 1979).

Livestock and poultry farming are sources of contaminants in water through the intensive management of grazing pasture and the operation of concentrated animal feeding operations (Mallin and Cahoon, 2003). Livestock farming produces waste containing many pathogenic micro-organisms associated with serious gastrointestinal disease, including bacteria such as *Escherichia coli* and *Streptococcus*, viruses such as enterovirus, and protozoa such as *Cryptosporidium* and *Giardia*. Not all strains (sic) of *E. coli* are harmful but some are serious pathogens (Fitts, 2002; Hiscock, 2005). Cryptosporidiosis is a significant cause of gastroenteritis in the United Kingdom with an estimated 42,000 cases in England and Wales in 1995 (Adak *et al.* 2002). Cryptosporidiosis is caused by the protozoan pathogen *Cryptosporidium parvum* found in the intestinal regions of most humans and animals, is excreted from infected individuals as an oocyst that can survive for long periods in the environment. The outbreaks of cryptosporidiosis (due to oocyst-contaminated groundwater supplied by wells) have occurred in karst limestone aquifers, for example the Edwards Aquifer

in Texas (Sweat *et al.* 1999) and the Chalk aquifer in the north London Basin (Willocks *et al.* 1999). *Cryptosporidium* contamination hazard assessment and risk management for British groundwater sources are discussed by Morris and Foster (2000). The adverse effects of agriculture on water quality can be reduced by sound management practices and optimum use of fertilizers, pesticides and irrigation water.

2.7.4 Ion exchange

Ion exchange reactions in aquifers can majorly influence the natural groundwater chemistry and is an important consideration in predicting the migration of contaminants such as heavy metals and polar organic chemicals (Hiscock, 2005). These reactions are sorption, adsorption, and absorption, desorption and base exchange. Sorption involves combination of two reactions adsorption and absorption. In adsorption case molecules or ions is attached or held to a solid surface while in absorption sobate enters (is incorporated) the mineral structure (Fitts, 2002). The natural materials which act as the most important adsorbants are clay minerals (are common), glauconite, and rock-forming silicates like zeolites, micas, feldspathoids and organic material like humus. Desorption is the release of molecules and ions from solid phase to the solute. Base or cation exchange occurs when an ion in solution gets sorbed to a surface and a similarly charged ion is released leading to adsorption of cations on mineral surfaces, (Singhal and Gupta, 2010).

Major ion exchange reactions also affect other constituents order than the exchanging ions, especially through dissolution and precipitation reactions. The attenuation of some pollutants, for example NH_4^+ , is mainly by the process of ion exchange (Carlyle *et al.* 2004). Ion exchange reactions can also lead to changes in the hydraulic conductivity of natural materials (Zhang and Norton 2002). The effect of cation exchange on groundwater quality due to rock lithology and movement of contaminants has been cited widely in groundwater literature such

as Back and Hanshaw 1965; Freeze and Cherry 1979; Hem 1989; De Marsily 1986; Kehew 2001 among many others. The affinity for adsorption is greater in ions with higher valence (that is, it is more difficult to remove ions of higher valence than that of lower valence) and for ions of the same valence, the affinity for adsorption increases with increase in the atomic number and ionic radius (Hiscock, 2002). The energy absorption sequence is: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ and this provides a general ordering of cation exchangeability for common ions in groundwater (Singhal and Gupta, 2010). The order indicates that at similar concentrations, ions will replace those ions which lie to their right.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Materials

3.1.1 Data Acquisition

Information on the aquifer type were obtained from topological and aquifer maps (WARDROP, 1986). The water constituents characteristics were measured and compared characteristics expressed in the Nigerian and world health standard for drinking water.

3.1.2 Field materials

The water sampling exercises were conducted using the following items: field notebook, digital camera, Garmin 72H global positioning system (GPS), Multi parameter Hatch kits of Tracer and Martin MI 806 combined meter, 500mL and 60mL high density polyethylene (HDPE) containers, Markers, masking tape, and nitric acid.

The field data collection was conducted in accordance with the International Atomic Energy Agency (IAEA) sampling procedures booklet for isotope hydrology. The fieldworks and Laboratory analysis were carried out in collaboration with Nigeria Hydrological Services Agency (NIHSA) under a regional project coded RAF7011 supported by IAEA. Water Sampling, in-situ measurements, preservation, packaging and transportation of samples to appropriate laboratory was carried out by the researcher along with the two supporting NIHSA Officials. Sampling was covered Sokoto, Kebbi, and Zamfara States of the Sokoto Basin. Water samples collected were complete representatives of the ground and surface water resources of the basin covering the CT and CI aquifer systems as well as the main drainage

networks of the basin. Samplings were designed such that comprehensive information about the environmental characteristics of the area was easily assessed. In line with the scope of study, surface and ground waters of the basin were sampled.

All sampling points were geo-referenced using Garmin 72H global positioning system (GPS). The physical parameters of water quality; (temperature, electrical conductivity (EC), pH, total dissolved solid (TDS) and salinity) were determined in-situ using Multi parameter HACH kits of Tracer combined instrument and Martin MI 806 combined meter. (Plate I).



Plate I:GPS, HACH KITS TOOLS, masking tape, marker, field note book and HDPE plastics containers.

The water samples were collected from surface and ground water from the Sokoto Basin using, 500ml, and 60ml high density polyethylene (HDPE) plastic containers. Marker and masking tapes were used for labeling.

3.1.3 Laboratory materials

In the Laboratory, ion Chromatography, flame photometer, multi-analyte photometer, atomic absorption spectrophotometer (AAS) and titration tools were used to measure cations, anions, trace and heavy metals from the water samples, (Plate II).



a) Multi-Analyte Photometer in use



b) Flame-Photometer



c) Titration on-going

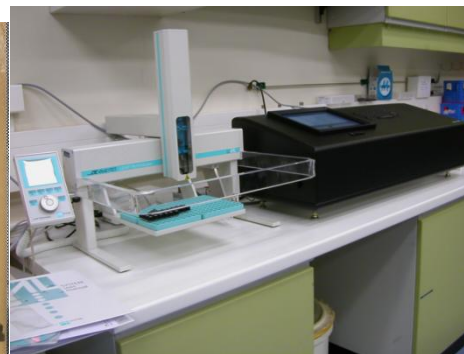


d) Atomic Absorption Spectrometer



For high activity measurements of alpha and beta emitting radioisotopes like tritium etc

e) Liquid Scintillation Counter



Laser Isotope Instrument

Plate II: Multi-analyte photometer, Flame photometer, Titration materials, Atomic Absorption photometer, Liquid scintillation counter and laser spectroscopic machine

These tools lists were used for calcium hardness titration: 10 and 20 mL pipettes, 250 mL conical flasks and 500 mL volumetric flasks and 100 mL measuring cylinders burette and stand.

Reagents used are: ethylenediaminetetraacetic acid (EDTA) 0.025 mol L⁻¹ solution, 2.0 mL of sodium hydroxide solution, 0.1-0.2g Patton-Reeder indicator, and 50 mL distilled water.

The radio-isotope data were determined using liquid scintillation counting, and stable isotope data were analyzed using mass spectrometer/ laser spectroscopic machine.

Analyses of hardness and heavy metals were carried out at the Center for Energy and Research (CERT), Multi-User Laboratory (MUSL) and Water Resources and Environmental Engineering (WREE) Laboratory respectively, Ahmadu Bello University, Zaria. Ions and Isotope data: oxygen-18, deuterium and tritium analyses were carried out at the Isotope Laboratory of the Centre National des Sciences et Technologies Nucléaires (CNESTEN), Rabat, Morocco.

3.2 METHODS

The process adopted in carrying out this research can broadly be divided into four main parts:

- I. Desk study of all available data
- II. Field data collection
- III. Laboratory data analyses
- IV. Results presentation and interpretation.

3.2.1 Desk study

The geological map of the area were digitized from the geological map of the Sokoto Region and borehole drilling reports obtained from the Sokoto Agricultural and Rural Development Authority (SARDA) and produced by WARDROP Engineering Consultants, Sokoto. The

hydrogeological information was obtained from Jones (1948), Parker (1964) Anderson and Ogilbee (1973), JICA (1990), Adelana *et al.*, (2003), Sokona *et al.*,(2008) and AzTech(2010), report. The demographic data and socio-economic activity on the other hand was partly obtained from the AzTech (2010), OSS(2008) and GEF(2003) and partly from field observations recorded in field note. WHO (2006) and SON(2007) (obtained from Nigeria Industrial Standard (NIS) documents) standard water quality criteria were used to determine present status of the water for drinking.

3.2.2 Field Data Collection Method

Eighty seven sampling sites were covered in two field sampling exercise carried out in July 2013 and April 2014 respectively. In the 87 sampling sites, there were 79 groundwater sample sites which were existing boreholes from the area and 8 surface water sample stations. Before a sample was taken, the position of the borehole was taken with a Garmin 72H GPS placed on the head of the borehole. The unit of measurement is degree decimal and World Geodetic System 84 (WGS 84) was used as a reference. Prior to sampling any well, some water samples from the well were collected and used to determine in-situ physical parameters such as pH, temperature, total dissolved solid (TDS), and Electrical Conductivity (EC). Four (4) different water samples were taken from each location. The type of analysis to be performed on the sample, the borehole ID and date of collection were indicated on the sample HDPE container (Plate I) for easy identification. The first water sample was collected in 60mL HDPE container for Tritium analysis; the second water sample was collected in 500mL HDPE container for D and ¹⁸O analyses; the third water sample was collected in 500mL HDPE container for cation analysis and the fourth water sample is collected in 500mL HDPE container for anion analysis.

i. Collection of Major Ion Samples

The samples for cation analysis were acidified with a 30% nitric acid (HNO_3) to reduce the pH to less than or equal to two ($\text{pH} \leq 2$) to avoid the precipitation of substances especially calcium. The 500mL HDPE containers each was used for collection of water sample cation and anion analyses. The containers were firmly capped and placed in a cool storage box.

ii. Collection of Stable Isotope Samples

The major precautions that were taken in the collection of the stable isotope samples was that, a representative water sample was obtained and the sample bottle filled to the brim. It was then firmly capped and stored in a cool storage box.

iii. pH Measurements

A Multi parameter meter was used in the measurement of the pH of the water samples. Before using the instrument for measurement, it was calibrated with standard solutions of pH 4.00 and 7.00. It was then rinsed with the water sample and dipped in the water sample until the pH readings remained stable. The accuracy of the measurement was ± 0.10 .

iv. Electrical Conductivity, Total Dissolved Solid and Temperature Measurements

The multi Hatch kit conductivity meter was used to measure the electrical conductivity of the water sample. It consists of a 6V alkaline-manganese, type AA battery-powered meter and a Hatch Tetracon 325 standard-conductivity cell. The instrument, after it was calibrated with a standard solution of 0.03M KCl, was rinsed with the water sample. The probe was dipped in the sample until the meter readings for conductivity and temperature remained stable.

3.2.3 Laboratory Analysis Method

The laboratory analyses in this study were divided into two parts namely:

- i. Major ions, minor ions and Heavy metals analyses
- ii. Stable deuterium (D) and oxygen 18 (^{18}O) and Unstable tritium (T) isotope analyses.

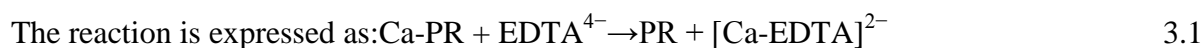
i. Major ions, Minor ions and Heavy Metals Analyses

The laboratory analyses of hardness and heavy metals were carried out by means of titration and Atomic Absorption Spectrophotometer (AA240FS-Varian) respectively. CHEMetrics V-2000 Multi-Analyte Photometer, supported by Photometric Test Kits like the Vacu-vials were used for anions analyses. Inductive couple plasma mass spectrometer (ICP-MS) and liquid scintillation counter was used for stable isotope analysis and tritium analysis. The cations and heavy metals measured were sodium ion (Na^+), potassium ion (K^+), calcium ion (Ca^+), magnesium ion (Mg^{+2}), boron (B), lithium (Li), silicon (Si), ammonium (NH_4), iron (Fe), lead (Pb), cadmium (Cd), and chromium (Cr); while the anions measured were chloride ion (Cl^-), bicarbonate ion (HCO_3^-), and sulphate ion (SO_4^{-2}), and nitrate ion NO_3^{-2} .

The AAS technique uses of absorption spectrometry to assess the concentration of an analyte in a sample. The electrons of the atoms in the atomizer were promoted to a higher orbit for an instant by absorbing a set quantity of energy (light of a given wavelength). This amount of energy (or wavelength) is specific to a particular electron transition in a particular element, and in general, each wavelength corresponds to only one element. As the quantity of energy (power) put into the flame is known, and the quantity remaining at the other side (at the detector) was measured. It is was possible to calculate how many of these transitions took place, and obtained a signal that was proportional to the concentration of the element measured. The result was then display in an attached computer monitor serving as an output device.

The calcium hardness was measured following the principle of complexometric titration principle being used in the laboratory where analysis was conducted. The method uses a very large molecule called ethylenediaminetetraacetic acid (EDTA) as well as Patton and Reeder's

indicator (a blue dye) which forms complex with calcium ions. But the dye–metal ion complex is less stable than the EDTA–metal ion complex. As a result, when the calcium ion–PR complex was titrated with EDTA the Ca²⁺ ions react to form a stronger complex with the EDTA.



The sample were thoroughly shaken, then, 25mL of the sample was diluted to 50mL with distilled water in a conical flask after which 2.0mL of NaOH solution was added and swirled, 0.1-0.2g of Patton-Reeder indicator was added and swirled to dissolve the indicator. The sample was then titrated with diluted ethylenediaminetetraacetic acid (EDTA) standard solution to a blue end point (Plate II). The hardness concentrations measured in milligram per liter (mg/L) were calculated from the moles of EDTA required to complex the Ca²⁺ ions in the sample using the following expression:

$$\text{Hardness} = \frac{A \times B \times 400.8}{\text{mL of sample}} \quad 3.2$$

Where, A is mL of titrant, B is mg of CaCO₃ to 1.00mL EDTA titrant and mL of sample.

The operation of the ion chromatograph is based on the well-established principle of ion exchange chromatography; and the use of electrical conductance in the determination of ions in solution after their initial separation. The equipment is made up of a dual eluent reservoir (A and B), pump, sample injection valve, a pair of guard and separator columns, dual Self Regenerating Suppressor (SRS) column, conductivity cell, conductivity meter and a recorder. When a sample is injected into the system, the pump elutes some eluent at the rate of 1mL/min to ensure that the sample was present in the electrolyte background. The eluents are mainly aqueous acids for cation analysis and aqueous bases for anion determination.

The sample in the eluent background is then moved into the separator column by passing it through the guard column. The double separators were switched on in turns in the analysis of either cations or anions. The separators were made of a low-capacity exchange separator resin, using strong acid for cation analysis and strong base for anion determination. The resins are stable over a wide range of pH. The Self-Regenerating Suppressors were used to convert relatively high conductive eluent ions into species of low or zero conductance so as to aid the conductivity cell to pick only the conductivity of the sample in question.

i. Sulphate ion measurement

Sulfate Vacu-vials for CHEMetric photometers (Multi-analyte photometer) was used. The sample cup was filled to 20mL mark with water sample. Then, seven drops of A-9200 Acidifier Solution was added to it, after which it was stirred properly to mix the content of the cup. A scoop of A-9202 Activator Powder was thereafter added and stirred to mix. Vacu-vial ampoule tip was then placed into the sample cup (containing mixture of the water sample, acidifier solution, and activator solution) where the tip was snapped, the ampoule was filled leaving bubble for mixing. The ampoule was inverted several times to mix and allowed for 1 minute before it was inserted into the photometer to obtain sulphate value in part per million (ppm). The Sulfate Vacu-vials test kit of CHEMetrics adopts the turbidimetric method of measurement of sulfate ion (APHA, 1980). Sulfate ion reacts with barium sulfate crystals of uniform size. The resulting turbidity is proportional to the sulfate concentration of the sample.

ii. Chloride measurement

Chloride Vacu-vials for CHEMetric photometers (Multi-analyte photometer) was also used. The sample cup was filled to 20mL mark with water sample. Using syringe, 1.0mL of A-2100 Activator solution was added and stirred to mix properly with the content of the cup. Vacu-vial ampoule tip was then placed into the sample cup (containing mixture of the water sample,

and activator solution) where the tip was snapped, the ampoule was filled leaving bubble for mixing. The ampoule was inverted several times to mix and allowed for 1 minute for color development before, it was placed flat end first into the photometer to obtain chloride value in part per million (ppm). The Chloride Vacu-vials test kit of CHEMetrics employs the ferric thiocyanate to liberate thiocyanate ion method of chloride ion measurement (Zall *et al.*, 1956; O'Brien, 1962; APHA, 2005). Ferric ion reacts with thiocyanate ion to produce an orange-brown thiocyanate complex in proportion to the chloride concentration.

iii. Nitrate Measurement

Nitrate Vacu-vials for CHEMetric photometers (Multi-analyte photometer) was used. The reaction tube was filled to 15mL mark with the water sample. Then, one Cadmium foil pack was emptied into the reaction tube containing 15mL of water sample for treatment. The reaction tube was capped and shaken for three minutes before; it was allowed to sit for two minutes undisturbed. The 10mL of treated in reaction tube was thereafter added to 25mL sample cup being careful not to transfer cadmium particles into the sample cup. Vacu-vial ampoule tip was then placed into the sample cup (containing treated water sample) where the tip was snapped, the ampoule was filled leaving bubble to facilitate mixing. The ampoule was inverted several times to mix and allowed color development for 10 minute before it was inserted into the photometer to obtain nitrate value in part per million (ppm). The Nitrate Vacu-vials test kit of CHEMetrics applies the Cadmium Reduction method of measurement of nitrate ion (APHA, 2005). Nitrate ion is reduced to nitrite in the presence of cadmium. In an acidic solution, the nitrite diazotizes with a primary aromatic amine and then couples with another organic molecule to produce a highly coloured azo dye. The resulting pink orange colour is proportional to the nitrate concentration. The results are expressed in ppm.

iv. Iron Concentration Measurement

Using the Iron Vacu-vials for CHEMetric photometers (Multi-analyte photometer), the sample cup was filled to 25mL mark with water sample with addition of five drops of A-6000 Activator solution and proper stirring to mix. It was allowed to sit for 4minutes before the tip of Vacu-vial ampoule was snapped in the sample cup containing mixture of treated sample with activator. The ampoule was inverted several times to mix and allowed for 1 minute before it was inserted into the photometer to obtain sulphate value in part per million (ppm). The Iron vacu-vials test kit of CHEMetrics employs the phenanthroline chemistry according to APHA (1998). Total iron is determined by adding a mixture of thioglycolic acid and ammonia to the sample. This mixture dissolves most forms of particulate iron. Results are expressed in ppm Fe.

v. Stable Isotope Measurements

The oxygen and deuterium isotope ratio were, carried out on a dual inlet isotope ratio mass spectrometer of Euro Vector instruments (PY; EuroPyrOH-3100) with a Euro Vector Elemental Analyzer (EA; Euro AS-300) and Gas Chromatograph coupled to a Micromass IsoPrime isotope ratio mass spectrometer (IRMS). The basic components of these analytical systems are illustrated in Figure 3.1.

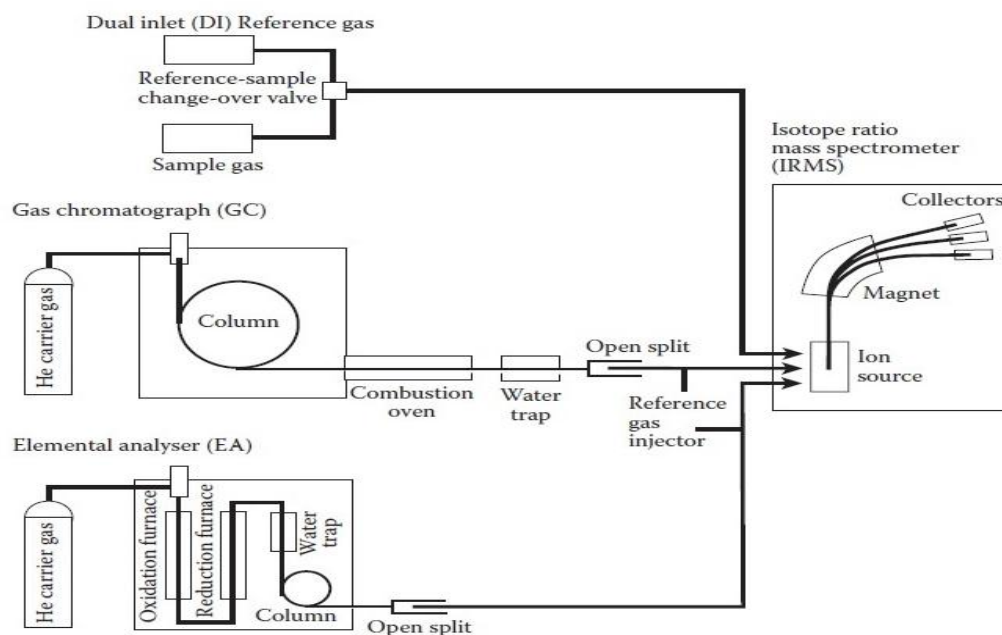


Figure 3.1: Schematic representation of a dual inlet isotope ratio mass spectrometer (DI-IRMS) diagram (Source: Aelion *et al.*, 2010).

For analysis of oxygen isotopes, no reaction was necessary since the isotope ratio can directly be measured in the form of O_2 , (Wassenaar and Koehler 1999). The O_2 was equilibrated between the aqueous phase and an initially O_2 free headspace(sic) and then the O_2 injected into a modified EA (Brand, 2002) or a GC-IRMS system (Roberts, *et al.*, 2000). In both cases, the O_2 was separated on a column from other gases before entering the IRMS. The molecules of oxygen were introduced in gaseous form into the ion sources in the IRMS see Fig 3.2 for enlarged section. They become ionized and travel through a magnetic field where they are deflected with a different radius making it possible to be detected in separate collectors of Faradays' cups. Thus, the abundance of small molecules of oxygen with different mass (^{16}O , and ^{18}O) was measured. The measurement of oxygen isotope ratios was carried out relative to the isotope ratio of oxygen reference gas, this rules' out potential mass discrimination during ionization or transfer of molecules (Epstein and Mayeda, 1953; Clark and Fritz, 1997). Then the isotope ratio was calculated from the ion ratio using the following expression:

$$\delta^{18}\text{O}(\text{‰}) = \frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{sample}} - \left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{standard}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}}\right)_{\text{standard}}} \times 1000 \quad 3.3$$

(Source: Kebede, 2012)

The reference standard is Vienna Standard Mean Ocean Water (VSMOW). If the δ value is positive, it points to the enrichment of the sample in the heavy-isotope species with respect to the reference and negative value corresponds to the sample depleted in the heavy-isotope species, (Mazor, 2004, and Kumar, 2010).

For Hydrogen isotope analysis, the pyrolysis unit analyzer-isotope ratio mass spectrometer (PY-IRMS), calibration and standardization was accomplished by measurement of standards of hydrogen before the samples are then heated at temperatures up to 1450°C in absence of oxygen (Gehre and Strauch, 2003) to liberate hydrogen gas. The hydrogen gas liberated was subsequently separated by gas chromatoph (GC) in the GC column and transferred to the IRMS for measurement as shown in Fig 3.2.

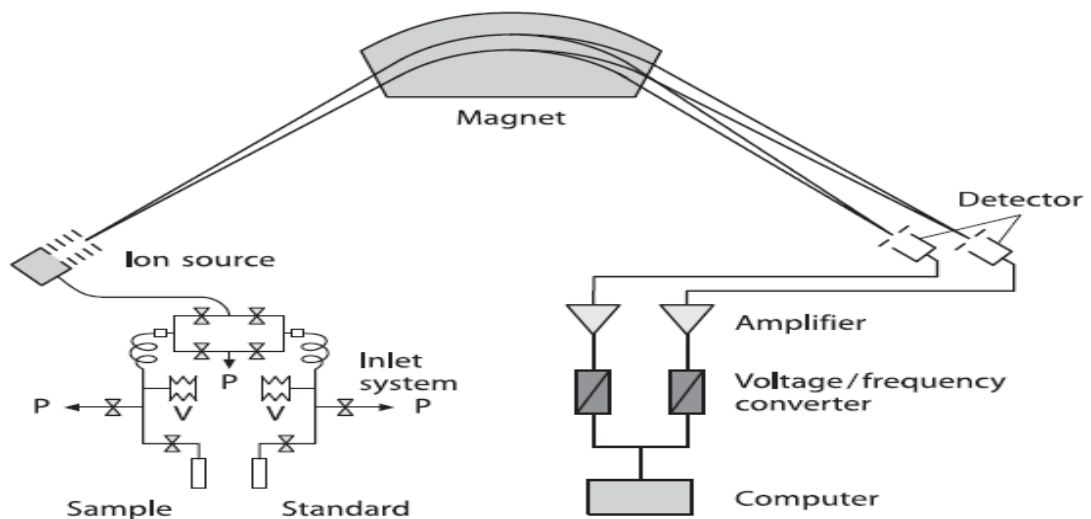


Figure 3.2: Schematic representation of a magnified IRMS section in Fig 3.1, P denotes pumping system, and V denotes a variable volume (Source, Hoefs, 2009).

With IRMS instrument, the hydrogen gas was introduced into the ion source where it became ionized and then travels through a magnetic field. The ions are deflected in separate collectors of Faradays' cups. The isotope ratio was calculated from the ion ratio using the following expression:

$$\delta^2H(\text{‰}) = \frac{\left(\frac{{}^2H}{{}^1H}\right)_{\text{sample}} - \left(\frac{{}^2H}{{}^1H}\right)_{\text{standard}}}{\left(\frac{{}^2H}{{}^1H}\right)_{\text{standard}}} \times 1000 \quad 3.4$$

(Source: Kebede, 2012)

Generally, the results for both isotopes are expressed in per mill (‰) relative to the Vienna Standard Mean Ocean Water (V-SMOW) to $\pm 0.3\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1.0\text{‰}$ for δD .

vii. Tritium Measurement:

In the experiment, water sample is purified by simple distillation (Figures 3.2 and 3.3) to separate the tritium-containing water from both non-radioactive and radioactive impurities, and the tritium beta particles in the condensate are measured with a liquid scintillation (LS) counter.

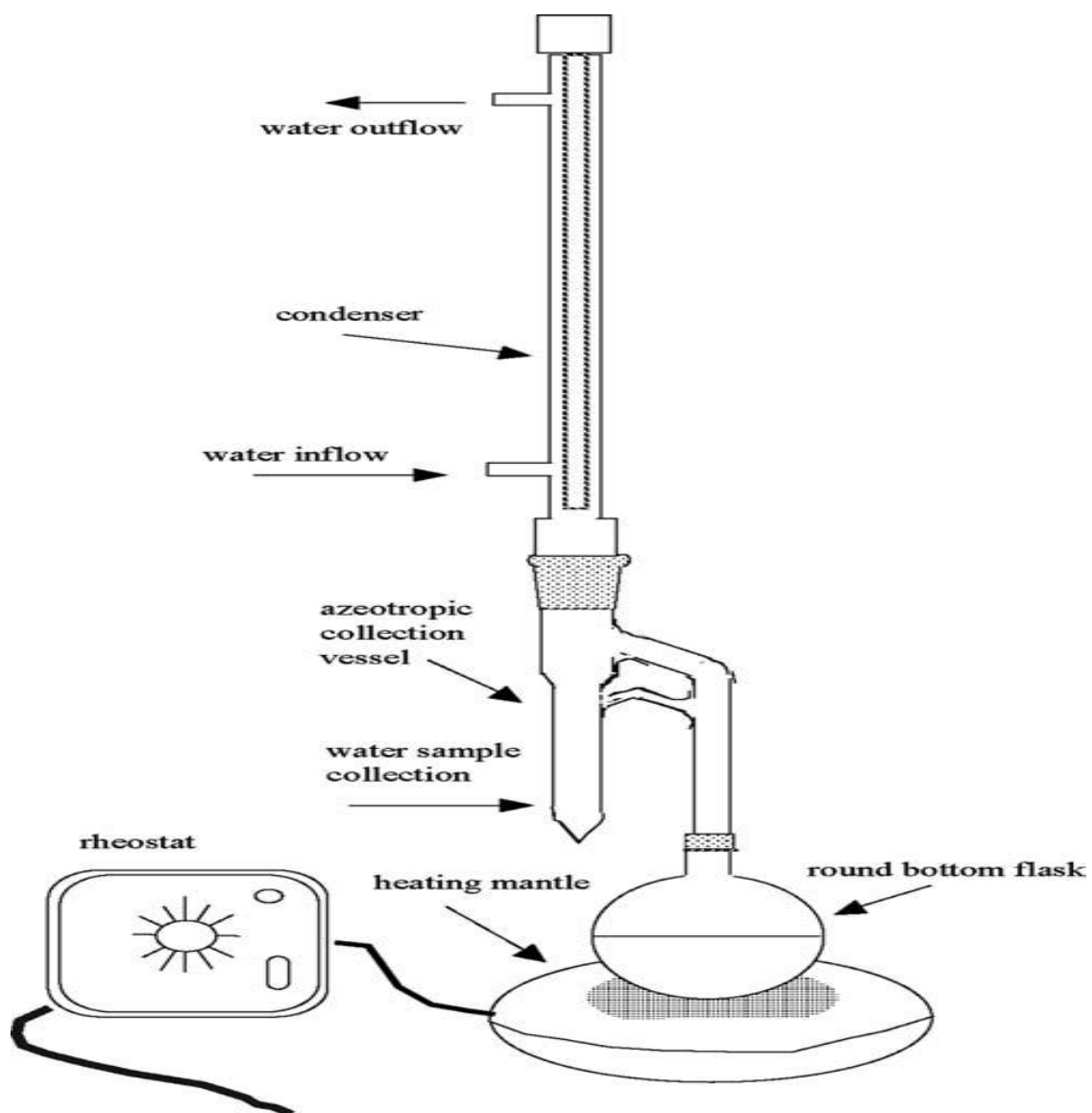


Figure 3.3: Distillation apparatus schematic (Source: Moses and Bernd, 2008)



Figure 3.4: Distillation apparatus (Source: Moses and Bernd, 2008)

An aliquot of the distilled and condensed tritium-containing water sample is prepared, for Liquid Scintillation (LS) counting by adding it to a LS cocktail in a counting vial. Also, the prepared sample vials are counted in the same batch with the vial of a standard tritium solution, and vial of a blank water solution. The tritium activity analyzed from the sample was calculated by subtracting the count rate in the blank sample from the gross count rate of the sample and the standard solution to obtain net count rates. The sample net count rate according to Moses and Bernd (2008) is then multiplied by the ratio of the standard solution activity to its net count rate to obtain the sample activity using the following equation:

$$A_{\text{sample}} = \frac{R_{\text{gross}} - R_{\text{bkg}}}{\epsilon_T} \quad 3.5$$

where, A_{sample} is activity of tritium in the sample, (TU); R_{gross} is gross count rate of the sample (cps), and R_{bkg} is average blank (background) count rate (cps), and ϵ_T counting efficiency for tritium.

$$\epsilon_T = \frac{R_{\text{gross}} - R_{\text{bkg}}}{A^0} \quad 3.6$$

Where, A° is disintegration rate (“activity”) of tritium in the standard sample (TU) and R_{gross} is gross count rate of the standard sample (cps). The results of the analyzed samples were reported in Tritium Unit (TU).

3.2.4 Data Processing and Result Evaluation Method

The combined softwares used for evaluation of test results included the PHREEQC of Aq.C 11, ArcGIS 10.1, Statistica 11, Sufer 10, and Global Mapper,

Palaeoclimatic conditions were assessed from the isotopic composition of groundwater samples taken from the water bearing formations using stable isotopes of $\delta^{18}\text{O}$, $\delta^2\text{H}$ and radioactive isotope of ^3H .

i. Data Processing

The concentrations measured in part per million (ppm) were converted to meq/L as required, (Fitts, 2002; Mazor, 2004, Singhal *et al.*, 2010) to enable further calculation for reaction error. Reaction error (RE) is another way to estimate data quality. The accuracy of chemical parameters of water samples were checked by calculating the cation–anion balance, expressed in meq/L. The percentage error or ‘ion-balance error’ (e), or reaction error (RE) or electron neutrality (EN) was determined following Matthes (1982) and Fitts (2002) method using the following equation:

$$RE = EN = e = \frac{\sum cation - \sum anion}{\sum ions} \times 100 = \frac{TC - TA}{TC + TA} \times 100 \quad 3.7$$

Where all ions are expressed in meq/L, with TC represents sum of cation expressed, TA represents sum of anion and RE is expressed in percent (%). Similarly, γC represents sum of cation and γA sum of anion in meq l^{-1} .

All solutions must be electrically neutral. In other words, the sum of cations equals the sum of anions in each solution. The deviation from such equality provides another way to assess data quality. The reaction error is thus expressed as a percentage of the total ion concentration.

ii. Statistical and Technical Evaluation Methods

In this study, range, mean, standard deviations are the descriptive statistical analyses carried out and least square regression was inference statistical approach applied.

The Degree of contamination (CD) was used as reference to estimate the extent of metal pollution (Al-Ami *et al.* 1987). It is computed using the equation given below (Kadarshahib *et al.*, 2015):

$$CD = \sum_{i=1}^n Cf_i \text{ where, } Cf_i = \frac{CA_i}{CN_i} - 1 \quad 3.8$$

Where, Cf_i is the contamination factor for the i th component; CA_i denotes the analytical value for the i th component; CN_i denotes the upper permissible concentration of the i th component (N denotes the “normative value”) (Ameh *et al.*, 2011).

The heavy metal evaluation index (HEI or MI) was computed following Hussain and Ahmad, (2002) adopted expression:

$$MI = \sum_i^n Ce_i \text{ where, } Ce_i = \frac{C_i}{MAC_i} \quad 3.9$$

Where MAC is Maximum Allowable Concentration of a metal and C_i is concentration of each observed metal.

Percent sodium (% Na), computation was conducted using the expression:

$$\%Na = \frac{Na^+ + K^+}{Ca^{2+} + Mg^{2+} + Na^+ + K^+} \times 100 \quad 4.0$$

Where, all the ionic concentrations are expressed in meq/L.

The term residual sodium carbonate was introduced by Eaton (1950) and it is obtained using equation:

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \quad 4.1$$

Where the ionic concentrations are expressed in meq/L.

Computation of Sodium Adsorption Ratio (SAR) was carried out using expression:

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+}+Mg^{2+}}{2}}} \quad 4.2 \text{ where all}$$

the ionic concentrations are expressed in meq/L.

Magnesium hazard (MH) is expressed as a ratio of Mg ion concentration to combination of Ca and Mg ions concentration, multiplied by 100 as shown below.

$$MH = \frac{Mg^{2+}}{Ca^{2+}+Mg^{2+}} \times 100 \quad 4.3$$

Also, all ionic concentrations are expressed in meq/L.

iii. Graphical Methods

The graphical methods employed in this study include Compositional diagrams, Piper plots Schoeller Semi logarithmic diagram, Wilcox plot and meteoric water line plot. The relationships between measured and calculated parameters were clearly noted by the use of Compositional diagrams or Scatter plots or bivariate plots. The diagram is used to test a theory that the two variables are related. Piper diagram displays the relative concentration of the major cations and anions (Hiscock, 2005; Singhal and Gupta, 2010). It consists of two separate triangular plots and a central diamond plot where the points from the two trilinear plots are projected. In the triangular plots, the axes run from 0 to 100 on each of the three sides. In the right triangle, the axes increase in a counter clockwise direction. The axis restarts to zero at each apex; in the left triangle, the axes increase in a clockwise direction restarting at zero at each apex. For each sample, there are three variables to determine the plotting position in each triangular plot, (Singhal and Gupta, 2010). The Schoellers'semi logarithmic diagram (Schoellers', 1955, 1962) also known as fingerprint diagram allows major ions of many samples to be represented on a single graph in which samples with similar pattern can easily be discriminated. The Schoellers'diagram shows the total concentration of major ions in log-scale.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 Evaluation of Calculated Reaction Error (RE)

As earlier stated in chapter three, reaction errors provides alternative to estimating data quality. In this study, the total dissolved cations ($TC^+ = Na^+ + K^+ + 2Mg^{2+} + 2Ca^{2+}$) and total dissolved anions ($TA^- = Cl^- + NO_3^- + 2SO_4^{2-} + HCO_3^-$) were well balanced within $\pm 10\%$ of the normalized inorganic charge balance (NICB). The reaction error as presented in Appendix, II ranged between -8.87% and 9.63% with a mean value of 2.65% . This is expected because according to Mazor (2004) the reaction errors in repeated measurements are expected to be random, this implies that, in part of the measurements the total cations will exceed the total anions and vice versa. Positive reaction errors noted in some cases reflect cation excess and negative errors in other cases indicate anion excess. Table 4.1 clearly showed that the results of the inorganic composition of water characteristics measured in the laboratory on 24.13% of representative water samples analyzed were accurate enough to be utilized for further processing and 75% of water samples have acceptable quality of data, (Fitts, 2002; Mazor, 2004; Younger, 2007; and Singhal and Gupta, 2010)

Table 4.1: Water quality evaluation using Reaction Error (RE).

Case study RE (%)	RE (%)	Interpretation
75.00	<5	Accurate for all uses
24.13	*5-10	Suitable for all uses
25.28	5-15	To be used with caution
0.00	>15	No serious scientific purpose

Note: Case study reaction error was extracted from Appendix.xi; * signify Singhal and Gupta specification.

According to Younger (2007), If RE value is less than 5%, then, the analysis can be regarded as sufficiently accurate for all uses. If RE lies in the range 5–15%, then the analysis should be

used with caution, while those analyses with RE values greater than 15% cannot really be regarded as being sufficiently reliable to justify using them for serious scientific purposes. Considering the analysed results high reaction errors ($>\pm 10$) were not recorded as such no data was omitted in further results processing. Generally, the results of this study are presented and discussed in two categories, results from measurements made in the field and laboratory (isotope data and hydro chemical data).

4.2 Field Measurements Results and Discussions

The physical properties of water such as temperature, pH, specific electrical conductance, total dissolved solid reflect its overall chemical behavior stated Younger, (2007). As such, the descriptive statistics summary of physical water properties measure in-situ for electrical conductivity (Cond), total dissolve solids (TDS), elevation (Ele), temperature (Temp), and pH for eighty seven water samples consisting of eight surface and seventy nine groundwater samples are presented fully in (Appendix III). Presented in Table (4.2) are the physical characteristics of representative sampled waters in the study area partly extracted from Appendix III.

Table 4.2: Physical constituents' of representative sampled waters measured in the Study area

Stn ID	Location	Sample ID	LAT(°)	LONG(°)	ELE (masl)	Temp(°)	pH	Cond (µS/cm)	TDS (mg/L)
SRES15	Rima river	GU	13.57	6.33	305	31	7	51	30
SRIS42	Rima River BK	GW	12.48	4.2	198	28	6.1	110	70
SRIS46	Argungu-Kangiwa Road	GW	12.74	4.52	209	29	6.6	100	60
SRI66	Balkori Bridge	SkG	13.29	5.21	261	32	6.15	490	310
GWSS25	Kandam	RmG	13.14	5.34	307	36	6.9	421	290
GWSS26	Hamma-Ali	RmG	13.17	5.34	322	35	7.1	578	400
GWSS55	Kebbe	RmG	12.13	4.72	223.3	32	4.7	420	260
GWSS56	Romom Sarki	RmG	12.21	4.6	217	33	5.48	60	30
Min					198	28	3.21	0	0
Max					530	40	7.53	2020	1280
Mean					279.0	32.48	5.75	343.31	228.39

masl= meters above sea level, Extn= extension, Lat=Latitude, Long= Longitude, Ele= Elevation, Cond= Electrical Conductivity, Temp= Temperature, Min=minimum value, Max=Maximum value, Mean= Arithmetic mean value, BK = Birnin Kebbi.

The overall physical characteristics of water (Elevation, Temperature, pH, Conductivity and TDS) ranged from 198.00masl to 530.00masl (mean=279.0masl), 28.00°C to 40.00°C (mean=32.48°), 3.21 to 7.53 (mean=5.75), 0.00µS/cm to 2020µS/cm (mean=343.31µS/cm) and 0.00mg/L to 1280mg/L (mean=228.39mg/L) respectively (see Table 4.2, Appendix. III).

The surface waters' physical characteristics (Elevation, Temperature, pH, TDS, and Conductivity) ranged 198.00masl to 305.00masl (mean=253.30masl), 28° C to 32°C (mean=29.88°C), 6.10 to 7.20 (mean=6.57), 30.00mg/L to 310.00mg/L (mean= 83.75mg/L) and 51.00µS/cm to 490.00µS/cm (mean=134.15µS/cm) respectively (see Table, 4.3).

Table 4.3: Physical constituents of sampled Surface water measured in the Study area

Stn.ID	Location	Sampl.ID	LAT (°)	LONG (°)	ELE (masl)	Temp (°)	pH	Cond (µS/cm)	TDS (mg/L)
SRES15	Rima river	GU	13.57	6.33	305.00	31.00	7.00	51.00	30.00
SRIS42	Rima River (Birnin Kebbi)	GW	12.48	4.20	198.00	28.00	6.10	110.00	70.00
SRIS46	Argungu- Kangiwa Road	GW	12.74	4.52	209.00	29.00	6.60	100.00	60.00
SRI66	Balkori Bridge	SkG	13.29	5.21	261.00	32.00	6.15	490.00	310.00
SRES18	Goronyo Dam	TA	13.49	5.88	287.00	29.00	6.60	78.80	50.00
SRIS27	Rima River(Illa Sokoto Road)	WU	13.12	5.24	242.00	30.00	6.74	98.00	60.00
SRIS28	Sokoto River	WU	13.08	5.26	274.00	30.00	7.20	65.40	40.00
SRES80	Shagari Dam	SkG	12.64	5.01	250.40	30.00	6.20	80.00	50.00
Min			12.48	4.20	198.00	28.00	6.10	51.00	30.00
Max			13.57	6.33	305.00	32.00	7.20	490.00	310.00
Mean			13.05	5.21	253.30	29.88	6.57	134.15	83.75

masl= meters above sea level, Extn= extension, Lat=Latitude, Long= Longitude, Ele= Elevation, Cond= Electrical Conductivity,Temp= Temperature, Min=minimum value, Max=Maximum value, Mean= Arithmetic mean value.

The ground waters' physical characteristics (Elevation, Temperature, pH, Conductivity and TDS) ranged from 206.00masl to 530.00masl (mean=282.09masl), 28.00°C to 40.00°C (mean=32.75°), 3.21 to 7.53 (mean=5.68), 0.00µS/cm to 2020µS/cm (mean= 364.50µS/cm)

and 0.00mg/L to 1280mg/L (mean=243.04mg/L) respectively as shown partly in Table 4.4, and fully in Appendix, IV.

Table 4.4: Physical compositions of representative sampled groundwaters in the study area

Location	Sample ID	LAT(°)	LONG(°)	ELE (masl)	Temp	pH	Cond (µS/cm)	TDS (mg/L)
Gwadabawa	SkG	13.34	5.23	266	33	6	1102	760
Gigane	SkG	13.49	5.23	256.7	31	5.72	1620	1040
Gidan Ciwake	SkG	13.72	5.29	265.1	38	5.3	1360	870
Wauru	SkG	13.76	5.49	334.5	40	5.5	1290	810
Rafin Duma	SkG	13.86	5.55	311.8	34	3.23	2020	1280
Taloka	RmG	13.44	5.69	287	31	5.4	1420	990
Gada	RmG	13.75	5.49	308.5	40	5.5	1290	810
Wurno(Kanwuru)	RmG	13.29	5.42	271	32	5.71	1172	810
Kandam	RmG	13.14	5.34	307	36	6.9	421	290
Hamma-Ali	RmG	13.17	5.34	322	35	7.1	578	400
Kebbe	RmG	12.13	4.72	223.3	32	4.7	420	260
Romom Sarki	RmG	12.21	4.6	217	33	5.48	60	30
				198	28	3.21	0	0
				530	40	7.53	2020	1280
				279	32.48	5.75	343.31	228.39

masl= meters above sea level, Extn= extension, Lat=Latitude, Long= Longitude, Ele= Elevation, Cond= Electrical Conductivity,Temp= Temperature, Min=minimum value, Max=Maximum value, Mean= Arithmetic mean value.

4.2.1 Total Dissolved Solid

In natural water bodies, dissolved solids includes particles that will pass through a filter with pores of around 2 µm (0.002 cm) in size and they consist of calcium, chlorides, nitrates, phosphorus, iron, sulfate, and other ions (Spellman, 2008). Likewise, total dissolved ions of the waters in this study as shown in Appendix II are by sum of the ions represented here by the mean concentration of various ions: calcium (1.60meq/L), magnesium (0.73meq/L), sodium (0.7meq/L), potassium (0.14meq/L), chloride (0.24meq/L), nitrate (0.36meq/L), sulfate (1.38meq/L), and carbonate (1.35meq/L). High concentration of total dissolved

solids(>1500mg/L according to SON (2007)) will make drinking water unpalatable and might have an adverse effect on people who are not used to drinking such water. In this study, the mean (228.39mg/L as in Table 4.4) concentration of TDS in the study is within (SON, 2007) permissible limit for drinking. Besides, the percent TDS characterization of waters in the study area (as in Table, 4.5) shows that 89.65% of the waters of the basin are suitable for drinking.

Table 4.5:TDS Characterisation of waters in the basin for drinking after (WHO, 2004)

Case study TDS (%)	TDS Standard (ppm)	Grade
89.65	<600	Excellent
5.74	600-900	Fair
3.44	900-1200	Poor
0	>1200	Unacceptable

This suggests that the waters are fit for human consumption and domestic use. However, 5.74% of waters of the basin were graded to be of fair quality, for example; Gwadabawa(760mg/L), Gidan Ciwake(870mg/L), Wauru(810mg/L), Gada(810mg/L), and Wuruno(810mg/L) were identified to fall within this category (see Tables 4.3 and 4.4). While, 3.44% were categorized as of poor quality, these stations: Gigane (1040mg/L), Rafin-Duma (1280mg/L) and Taloka (990mg/L) have TDS concentration within this class and 0% of unacceptable potability grade of TDS was recorded. It is pertinent to note that high TDS concentration (>600mg/L) were recorded groundwaters. Sources of total dissolved solids in water bodies involves' geogenic and anthropogenic origine. According to (Nti, 2005) the chemistry of groundwater of high TDS greater than 1000 mg/L is controlled mainly by evaporation while TDS of between 100 and 1000 mg/l derives its composition from its

interaction with rock units and TDS of less than 100 mg/L emanate from direct rainfall. Therefore, Figure 4.1 shows that 72.1% of the groundwater solutes originate from dissolution of aquifer material, while 25.9% of groundwaters reflect solutes from rainfall and 2.0% from evaporation. These suggests that majority of the groundwater in the study area probably acquired their chemical character by interacting with the aquifer materials while few of them from rainfall and evaporation.

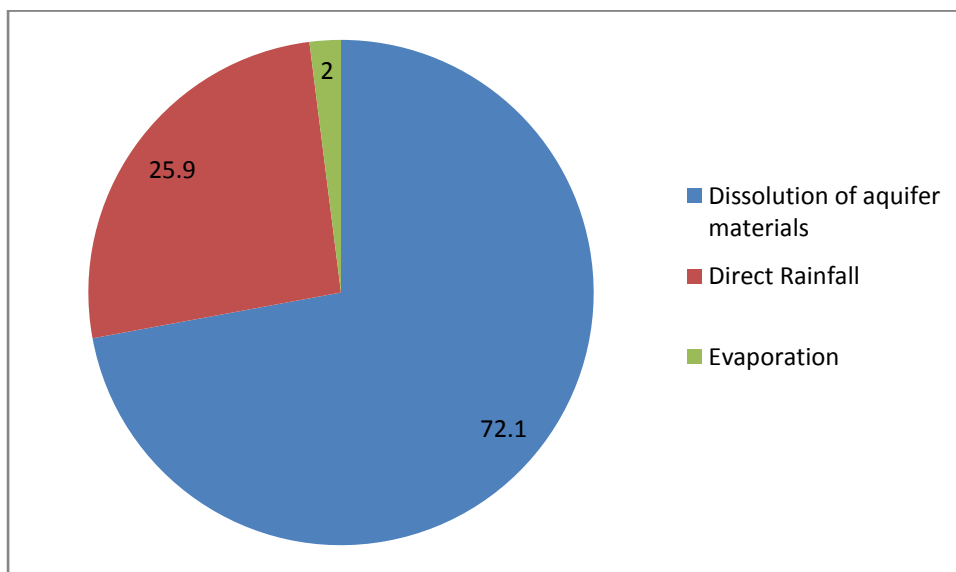


Figure 4.1: Control factors of TDS in the study area in percent (%)

Majority of the water samples in the area have TDS of less than the permissible level of 1000 mg/L for drinking water (WHO, 2004), irrespective of the Formation type except for a few, whose total dissolved solids concentrations are above 1000mg/L probably due to evaporation effect, and agricultural impact. Generally, total dissolved solids concentrations in groundwater increase as it moves from the surface to the saturated zone and through the aquifer because of the dissolution of minerals (Freeze and Cherry, 1979). Similarly, in this study, the 72.1% TDS distribution of controlling dissolve solid input in the basin indicates that the groundwater TDS

input is mainly from dissolution of minerals. In water distribution systems, a high TDS means high conductivity (Spellman, 2008).

4.2.2 Electrical Conductivity

Electrical conductivity measurements gave a rapid approximation of the concentration of dissolved solids. Presented in Figure.4.2, is a composite plot of electrical conductivity against total dissolved solid.

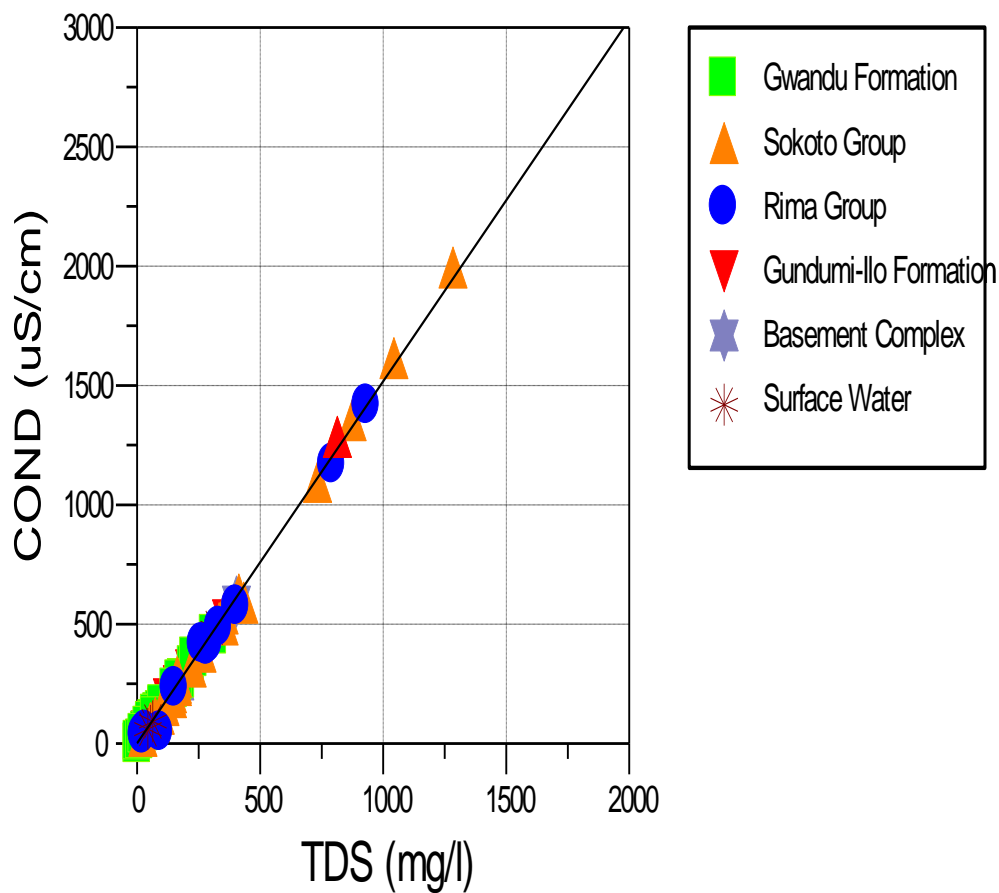


Figure 4.2: A plot of EC ($\mu\text{S}/\text{cm}$) versus TDS (mg/L) in the study area

The mean values for EC in waters of Sokoto Basin reflect waters suitable for domestic purpose since it is within acceptable standard requirement of SON (2007) EC specification of 2500 $\mu\text{S}/\text{cm}$ for drinking. Like TDS, EC is a function of the concentrations of all ionic solutes. As such, the plot of EC against TDS displayed expectedly a linear empirical correlation of electrical conductivity to TDS; see (Fig. 4.2). Moreover, the high EC values were observed mostly in Sokoto and Rima Group at similar locations where TDS values were high (Gwadabawa, Taloka and Wurno parts of the Sokoto Basin). Fitts (2002) stated that conductivity concentration ranging from 10 to 50 $\mu\text{S}/\text{cm}$ reflects solutes from rainfall while that from 150 to 1000 $\mu\text{S}/\text{cm}$ indicates increase in the total solute content due to dissolution of common minerals and that greater than 1000 $\mu\text{S}/\text{cm}$ reflect possible presence of marine water intrusion. Figure 4.3 shows percentage distribution of categorized conductivity concentration following Fitts (2002) classification.

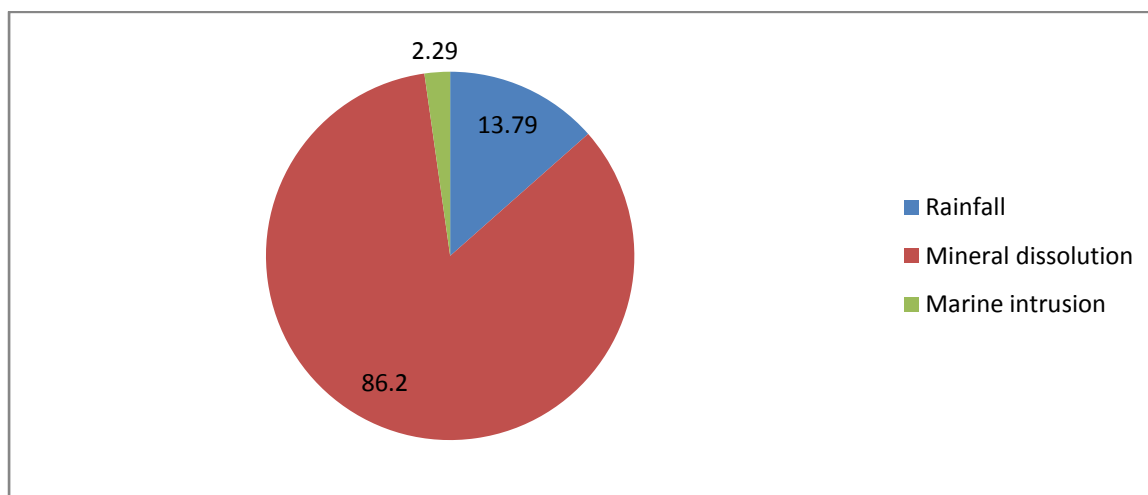


Figure 4.3: Percentage distribution of waters conductivity concentration

Figure 4.3 clearly showed that high conductivity of surface waters and groundwaters within the range 10–50 mg/L reflects paucity of solutes from precipitation. 86.2% of conductivity concentration in surface and groundwaters were sourced from dissolution of minerals from the soils and rocks that the water flows through. Also, the conductivity and TDS of groundwater

were noted to be higher than the TDS of surface waters. This is because, compared to surface water, groundwater contacts a much larger mineral surface area for a much longer time.

4.2.3 Elevation Feature

The elevations in the study area range from 206.00masl to 530masl (mean=279.43masl). Lowest elevations occur at Karama Damba Community by the South of the study area and the highest value at Gidan Gado North of the Study area. The superimposition of elevations of sampled points on the digital elevation model (DEM) of the study area showed a close match which is also an indication of true measurement of elevation (Fig.4.4), (Appendix, V)

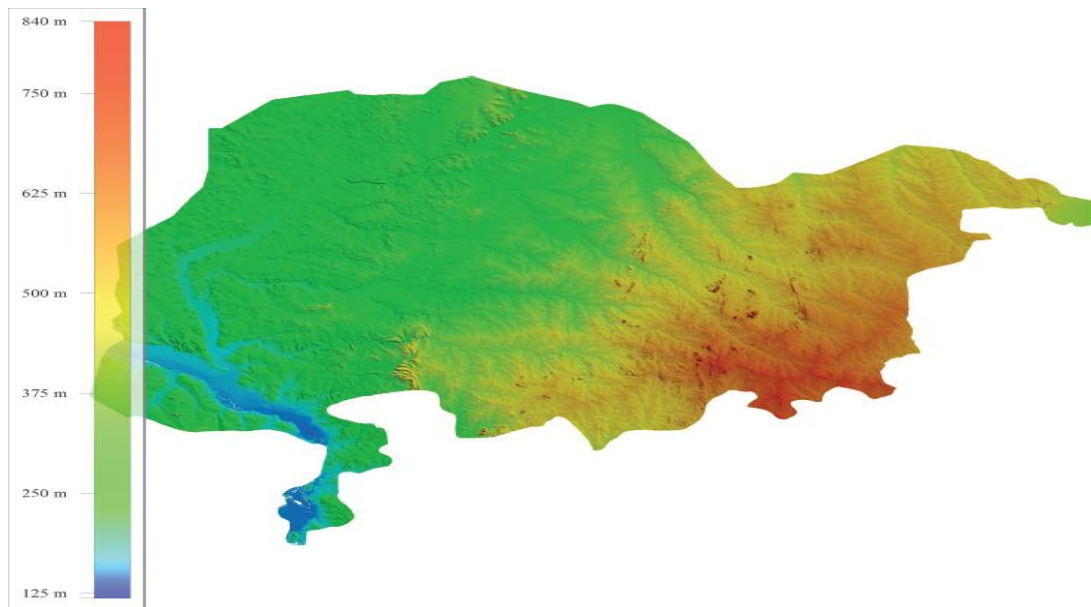


Figure 4.4: Digital Elevation Model DEM of the Study area

The superimposed water table contour on base map of the basin shows that the water table is shallower in the northeastern part of the study area and is deepest in the northwestern part (Figs. 4.5-4.7), (Appendices, VI-VII).

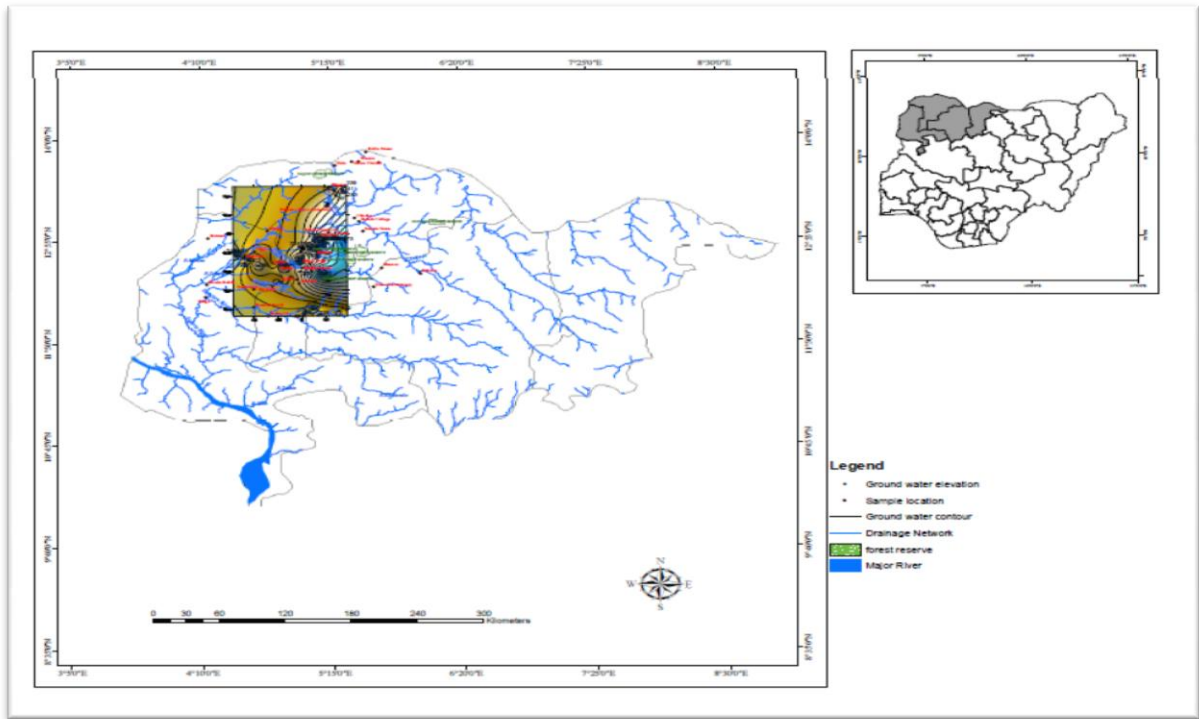


Figure 4.5: Superimposed water table contour map on sampled locations of study area (see Appendix VI)

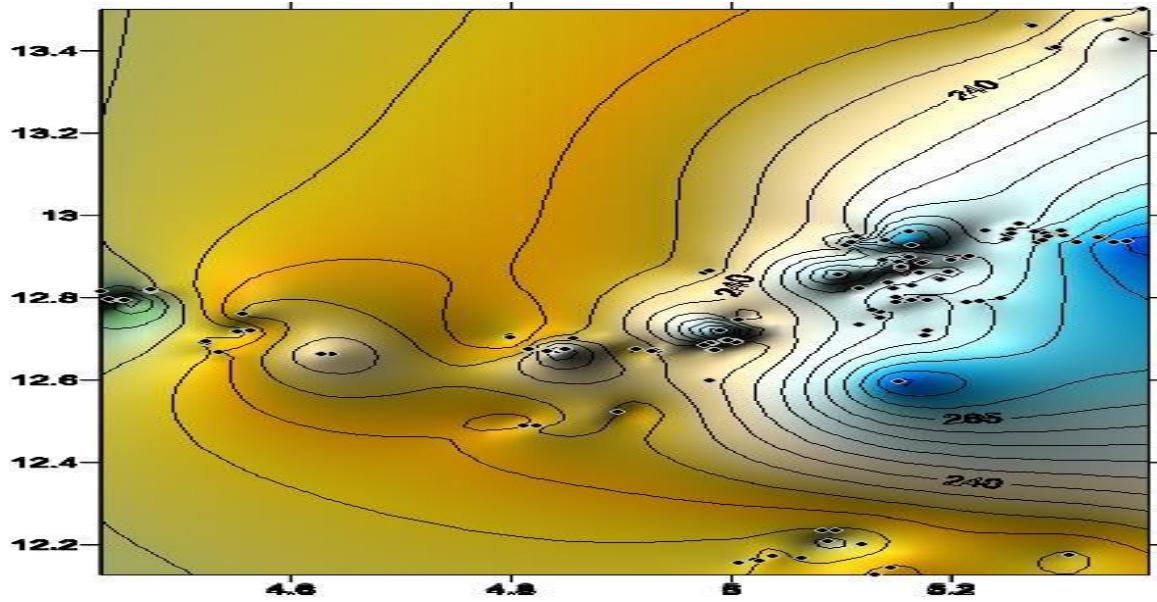


Figure 4.6: Delineated water table contour map of sampled locations (see enlarged copy in Appendix VII)

This indicates that the main drainage axes of the groundwater water table of the basin, is oriented northeast-southwest and northwest-southeast, Figure 4.7and Appendix VIII

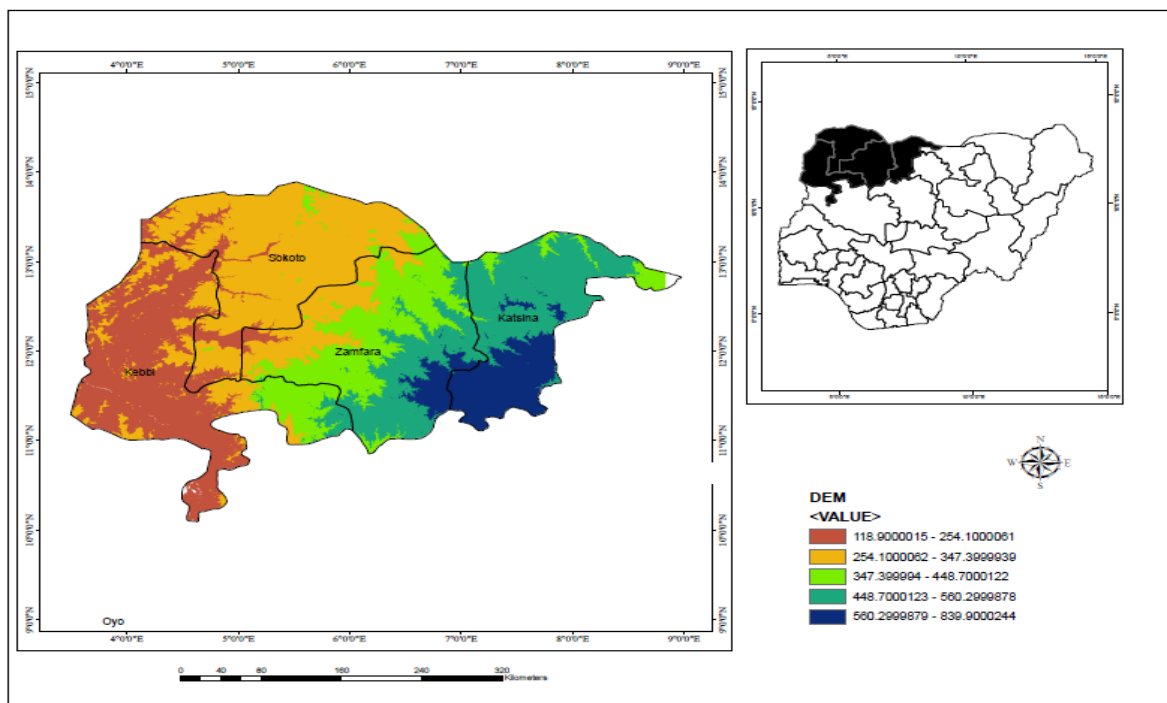


Figure 4.7:Superimposed elevation of study area on DEM map of the basin (Find in Appendix VIII, the magnified copy)

The result from this study conformsto the previous findings in the study area. OSS (2008), reported that in Iullemeden aquifer system, groundwater flows mainly from the northwest, north and northeast towards the south. Anderson and Ogilbee,(1973) showed that the headwaters of the Rivers Sokoto and Rima and their tributaries rise in pre-Cretaceous crystalline rock terrain east of the Sokoto Basin and flow west and south across a terrain underlain by sedimentary rocks of the Gundumi-Ilo Formation, the Rima and Sokoto Groups, and the Gwandu Formation.Also, the geological map superimposed on the base map of the study area (Figure 4.8 and Appendix.IX) showed the lithological composition of the formation types.

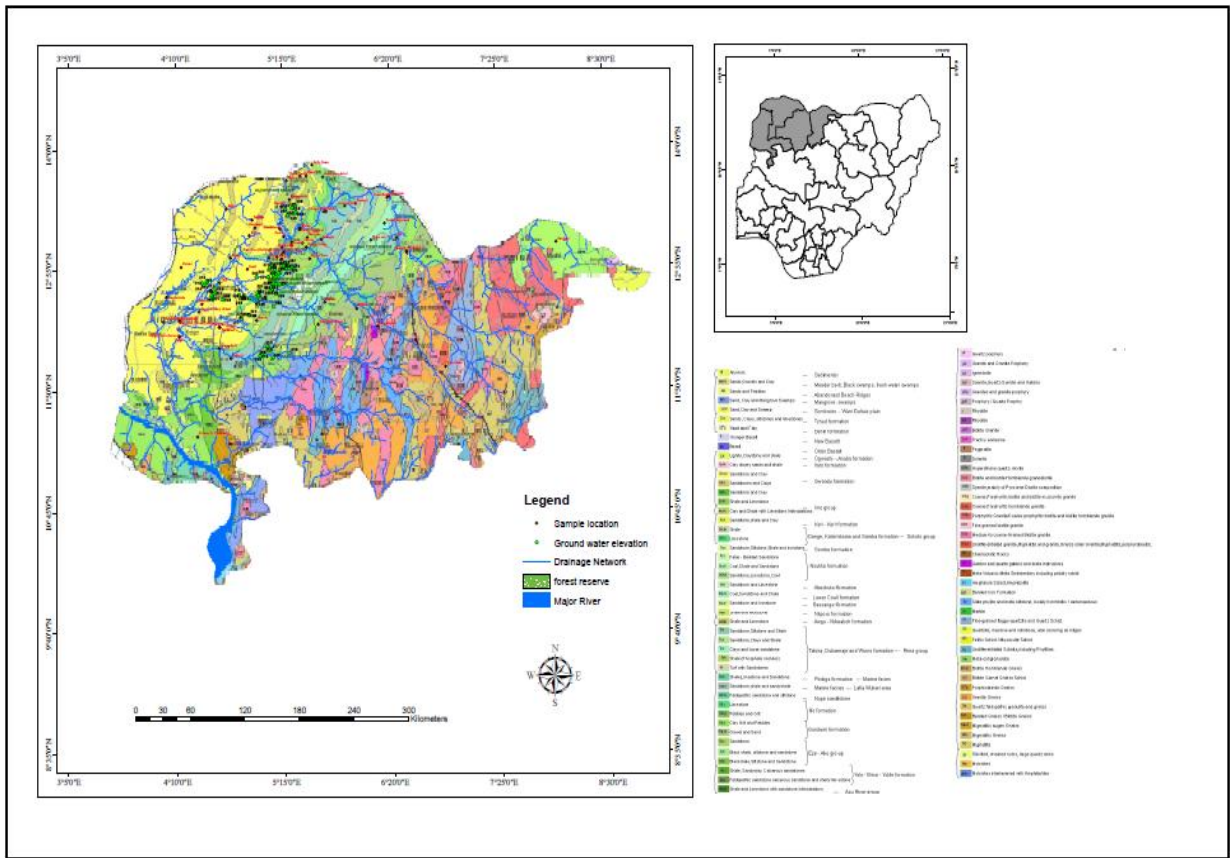


Figure 4.8: Geological map superimposed on the base map of the study area (Find copy of magnified map in Appendix IX)

4.2.4 Temperature

In this study no relationship was found between groundwater temperature and depth (Fig. 4.9) probably because data on borehole depths were scanty. It may be attributed to non homogeneity in aquifer characteristics state Nti (2005) in a related study. However, Bebout and Gutierrez (1981) observe that, the temperature of groundwater in South Louisiana, USA, increases with depth. More erratic temperature against depth profiles observed in Fig 4.9 may also reflect areas of mainly indirect recharge due to preferential flow paths could rapidly introduce cool recharge waters to depths at which surrounding, directly sourced recharge has already attained warmer temperatures, (Younger, 2007).

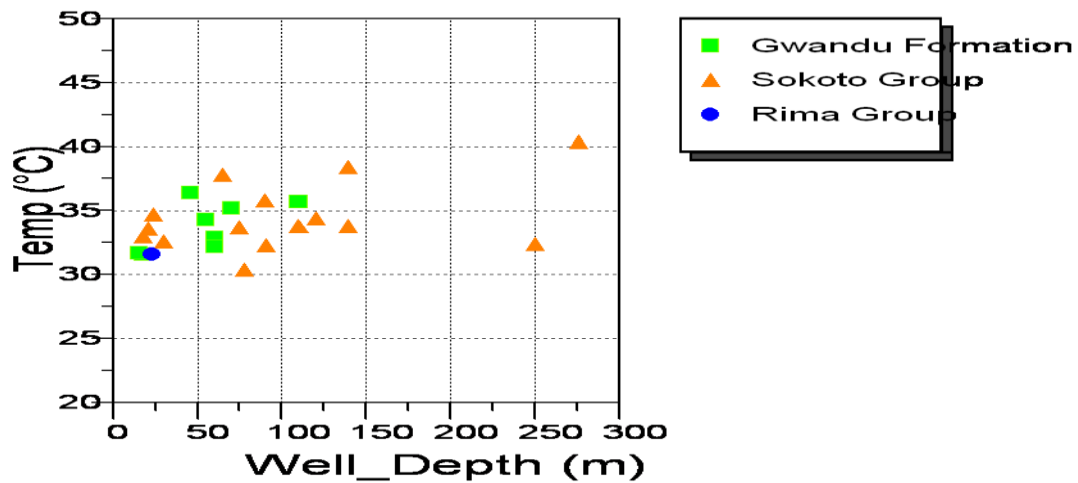


Figure 4.9: Composite plot of water temperature against well depth

Also, the mean temperature values of 32.48°C recorded is within the acceptable limit of SON (2007) that recommends ambient temperature for groundwater within its locality.

4.2.5 pH

Groundwater pH is a fundamental property that describes its acidity or alkalinity and largely controls the formation of many organic and inorganic substances dissolved in groundwater (Derickson, 2003). The waters are generally moderately acidic to slightly basic, with pH ranging from 3.21 to 7.53 (mean=5.75). Evaporative concentration may have contributed to significantly lower pH. On this basis, it may be expected that most fresh recharge waters would be relatively acidic (pH of 5 or less) (Younger, 2007). The surface waters' pH values ranged from 6.10 to 7.20 (mean=6.57±0.4) reflecting the peculiar nature of surface water pH grade (which is slightly basic) with a pH value of about 8 according to Younger (2007). The groundwater pH value ranged from 3.21 to 7.53 (mean=5.67±0.83) indicating possibility of acid rain which usually is characterized by low pH value of 4 (Younger, 2007). Relative,

low conductivity ($<500\mu\text{S}/\text{cm}$) and low pH (<7) as observed in Figure (4.10) denote short groundwater residence time (Helstrup, 2006).

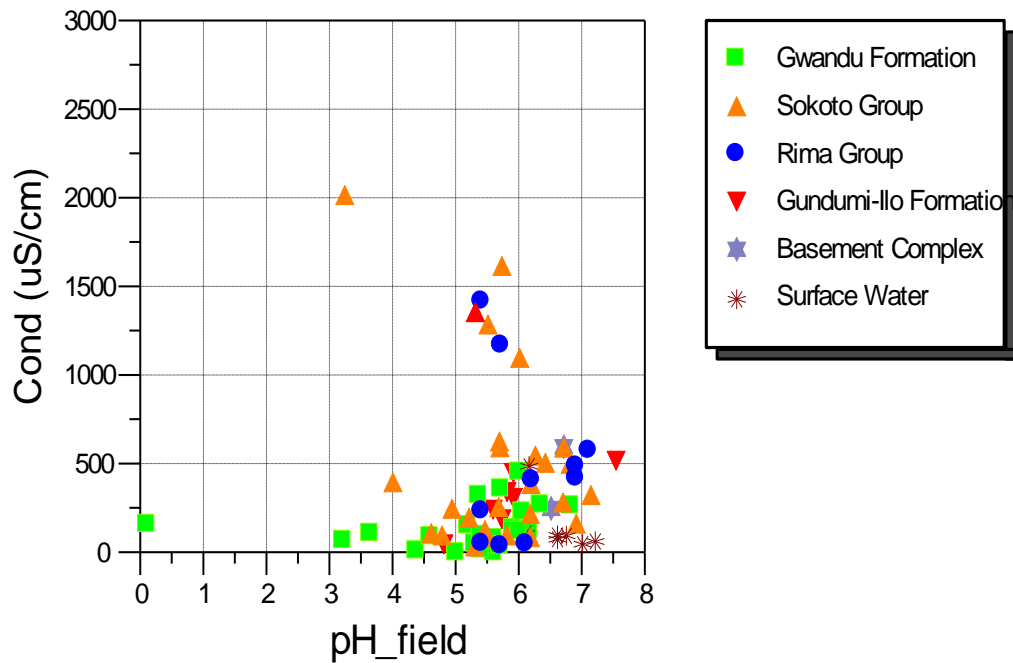


Figure 4.10: Scatter plot of Conductivity versus pH in the study area

Despite the moderately acidic nature of most of the samples, they fall within the pH range of natural water that is from 4.5 to 8.5 (Hounslow, 1995; Langmuir, 1997). However, 54% of the samples fall below the lower limit of the recommended range (6.5-8.5) for domestic use (WHO, 2006). Richardson (1991) noted that low pH levels obtained in well waters may be traced to the acidity produced by organic wastes decomposing under partially reducing conditions into organic acids. Related results were also obtained by Longe and Kehinde (2005); Yusuf, (2007); Glenn, (2008), Akudo *et al*(2010) and Longe and Balogun (2010). The effects of acidic waters on human health and the environment have been widely

reported. For example acidic waters have been known to be hard and enhance the dissolution of iron and manganese (Edwards *et al.*, 1983).

4.3 Results of laboratory Measurements

The laboratory measurements results in this study were classified into common environmental isotope and hydro-chemistry water results.

4.3.1 Environmental Isotopes Results of water molecule ($\delta^2\text{H}$, $\delta^{18}\text{O}$, ^3H)

The general range of $\delta^{18}\text{O}$ (-7.72‰ to 3.69‰), $\delta^2\text{H}$ (-51‰ to 9.42‰) and ^3H (-3.89TU to 4.9TU) values of the investigated water samples are shown in Appendix, X; Table 4.6.

Table 4.6 Isotope composition of representative sampled waters in the study area

Station Code	Location	Sample Code	^{18}O (‰)	^2H (‰)	^3H (T.U)	D-excess
SRES15	Rima river	GU	-2.47	-14.84	3.25	4.92
SRIS42	Rima River (Birnin Kebbi)	GW	-1.05	-4.62	2.54	3.78
SRIS46	Argungu-Kangiwa Road	GW	-1.93	-12.12	3.26	3.32
SRES80	Shagari Dam	SkG	3.69	9.42	4.1	-20.1
SRI66	Balkori Bridge	SkG	-1.08	-11.95	4	-3.31
SRES18	Goronyo Dam	RmG	-1.93	-9.49	2.88	5.95
SRIS27	Rima River (Illa Sokoto Road)	RmG	-1.54	-12.6	3.27	-0.28
SRIS28	Sokoto River	RmG	-3.49	-21.3	2.65	6.62
GWSS19	Taloka	RmG	-2.05	-12.75	1.42	3.65
GWSS20	Goronyo Town	RmG	-6.51	-48.26	-0.01	3.82
GWSS1	Kware	RmG	-3.69	-23.44	3.43	6.08
GWSS79	Yabo (Torankawa)	RmG	-4.39	-26.81	2	8.31
GWSS74	Bancho	RmG	-4.84	-26.27	<0.4	12.45
GWSS72	Gada	RmG	-2.11	-13.52	3.6	3.36
GWSS22	Wurno	RmG	-4.61	-34.3	0.06	2.58
GWSS23	Wurno (Kofar Rima)	RmG	-6.78	-48.31	-0.06	5.93
GWSS24	Wurno (Kanwuru)	RmG	-5.15	-36	-0.27	5.2
GWSS25	Kandam	RmG	-6.76	-46.28	-0.08	7.8
GWSS26	Hamma-Ali	RmG	-6.86	-45.56	0.24	9.32
GWSS55	Kebbe	RmG	-4.32	-24.5	3.1	10.06
GWSS56	Romom Sarki	RmG	-4.66	-26.73	1.7	10.55
Min			-7.72	-51.43	-3.89	-20.1
Max			3.69	9.42	4.9	14.39
Mean			-4.46	-28.04	1.55	7.63

‰= permil, TU= Tritium unit, Min=Minimum, Max=Maximum, Mean= Arithmetic mean

These results are consistent with related previous studies (McKenzie *et al.*,2001; Alagbe, 2004; Adelana *et al.*, 2004; Kebede *et al.*, 2005; Rodgers *et al.*, 2005; Demlie *et al.*, 2007, 2008; Ayenew *et al.*, 2008; Kebede *et al.*, 2008; Fehdi *et al.*, 2011; Adomako *et al.*, 2011; Bouragba *et al.*, 2011; Al-Gamal, 2011; Bretzler *et al.*, 2011, Wassenaar *et al.*, 2011 among many other).

The Surface water isotope signature of oxygen-18, deuterium and tritium compositions of waters in the Basin ranged from -3.49‰to3.69 ‰, -21.30 ‰to 9.42 ‰ and 2.54 to 4.10 TU respectively (Table 4.7).

Table 4.7 Isotope compositions of the examined surface water in the Basin

Stn. ID	Location	Sample ID	¹⁸ O (‰)	² H (‰)	³ H (T.U)	D-excess (‰)
SRES15	Rima river	GU	-2.47	-14.84	3.25	4.92
SRIS42	Rima River (Birnin Kebbi)	GW	-1.05	-4.62	2.54	3.78
SRIS46	Argungu-Kangiwa Road	GW	-1.93	-12.12	3.26	3.32
SRES80	Shagari Dam	SkG	3.69	9.42	4.10	-20.10
SRI66	Balkori Bridge	SkG	-1.08	-11.95	4.00	-3.31
SRES18	Goronyo Dam	RmG	-1.93	-9.49	2.88	5.95
SRIS27	Rima River(Illa Skt. Road)	RmG	-1.54	-12.60	3.27	-0.28
SRIS28	Sokoto River	RmG	-3.49	-21.30	2.65	6.62
Min			-3.49	-21.30	2.54	-20.10
Max			3.69	9.42	4.10	6.62
Mean			-1.23	-9.69	3.24	0.11

Abbreviation definition: ‰= permil, TU= Tritium unit, Min=Minimum, Max=Maximum, Mean= Arithmetic mean

The ground water oxygen-18, deuterium and tritium isotopic compositions of water in the Sokoto Basin ranged from -7.72‰ to -2.05‰ (mean= -4.78‰±1.23 ‰), -51.43‰ to -12.75‰ (Mean= -29.9‰±8.89 ‰) and from -0.3 to 4.10T.U (mean=1.02±1.45 TU) respectively (Appendix XI, Table 4.8).

Table 4.8 Groundwaters isotope compositions of the representative investigated waters

Station Code	Location	Sample Code	^{18}O (‰)	^2H (‰)	^3H (T.U)	D-excess(‰)
GWSS49	Kuka Mairafu	BA	-4.05	-25.42	1.95	6.98
GWSS50	Gidan Gado	BA	-4.19	-27.29	2.76	6.23
GWSS9	Gundumi	GU	-5.73	-32.87	0.11	12.97
GWSS87	YarGeda	GU	-4.85	-28.01	0.5	10.79
GWSS86	Bimasa	GU	-5.07	-30.36	<0.4	10.2
GWSS78	Ganbuwa	GW	-3.99	-26.46	1.9	5.46
GWSS64	Silame	GW	-5.53	-29.92	<0.4	14.32
GWSS2	Binji	GW	-5.05	-29.99	3.43	10.41
GWSS17	Tsamaye	SkG	-4.32	-25.79	2.93	8.77
GWSS21	Marnona	SkG	-3.92	-19.84	2.72	11.52
GWSS29	Wammakko	SkG	-5.27	-31.22	-0.37	10.94
GWSS30	Kalambaina Pri.Sch	SkG	-3.56	-21.69	2.89	6.79
GWSS74	Bancho	RmG	-4.84	-26.27	<0.4	12.45
GWSS72	Gada	RmG	-2.11	-13.52	3.6	3.36
GWSS55	Kebbe	RmG	-4.32	-24.5	3.1	10.06
GWSS25	Kandam	RmG	-6.76	-46.28	-0.08	7.8
Mean			-4.79	-29.91	1.34	8.39
Min			-7.72	-51.43	-3.89	1.23
Max			-2.05	-12.75	4.90	14.39

Abbreviation definition: ‰= permil, TU= Tritium unit, Min=Minimum, Max=Maximum, Mean= Arithmetic mean

The various processes (such as evaporation from the oceans, re-evaporation and runoffs) water undergoes before reaching its final destination underground impacts distinctive isotopic signature to groundwater and help in the study of environmental factors(sic) that affect surface and groundwaters (Mazor, 2004). Due to this property,environmental isotopes have become an invaluable tool in groundwater investigationsand serves as a conservative tracer of water origin (Hiscock, 2005).

4.3.2 Distribution and Trends in Stable Isotope Data in Sokoto Basin

The box and whisker plot of isotope composition of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ are presented in Figs. (4.11 and 4.12).

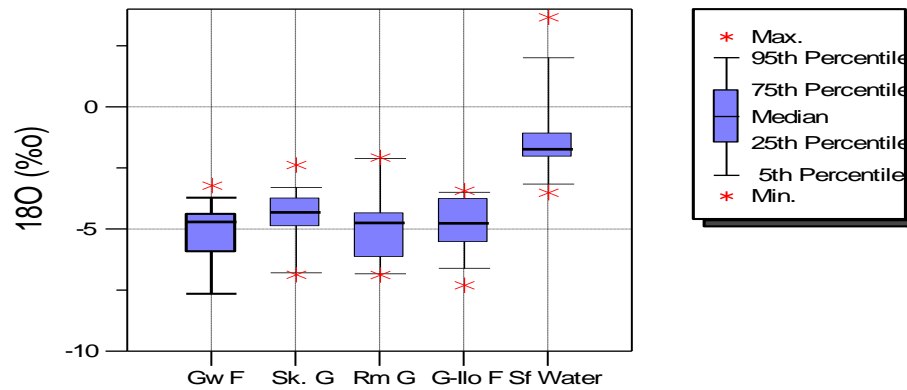


Figure 4.11: Box plot for $\delta^{18}\text{O}$ isotope composition of water types in Sokoto Basin.

Inspection of the boxplots for $\delta^{18}\text{O}$ for the various aquifer types shows that the most enriched data are those of surface water and Rima Group (RmG) respectively while the most depleted are well water samples tapping Gwandu Formation (Gw F); Sokoto Group (SK G) and Gundumi-Ilo Formation (Guile. F). The observed variabilities in the isotope signature may be related to the variations in the conditions prevailing at the various sampled locations like seasonal influence. It is also clear that the eighty seven representative samples of the ground and surface water data were taken during the start of the rainy season (July, 2013) and end of the dry season in April 2014 in the Sokoto Basin.

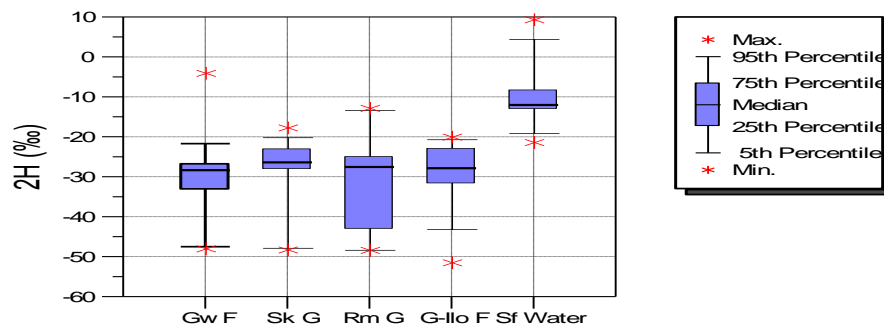


Figure 4.12: Box plot for $\delta^2\text{H}$ isotope composition of water types in Sokoto Basin.

As such, the observed variability may be partly attributed to seasonal effects. Also, the nature of water sampled, spatial locations, among others are partly responsible for the observed pattern of isotope signature measured in surface and ground water reported Bouragba *et al.*, (2011).

4.3.3 Hydro-Chemical Results

Generally, the concentration of ions dissolved in water is expressed in a variety of ways: Weight per volume (milligram per liter (mg/l) and microgram per liter ($\mu\text{g/l}$)), Weight per weight (grams per kilogram (g/kg) and milligrams per kilogram (mg/kg)) and Ionic equivalence units (equivalent per million (epm) and milligram equivalents per liter (meq l^{-1})). It is the consensus of the previous researchers that for the discussion of chemical processes it is most meaningful to express chemical data in ionic equivalence units, or equivalents (Fitts 2002; Mazor, 2004; Hiscock, 2005; Singhal and Gupta, 2005 etc.). A unit which is more convenient for geochemical studies is equivalent per million (epm) or milligram equivalents per liter (meq /L), (Singhal and Gupta, 2010). Milliequivalent per volume units, (meq/l), is used for cation and anions concentrations while heavy metals and other elements are expressed in milligram per liter (mg/L) in this study.

4.4 Chemical Composition and Characterization of waters of the Basin

In order to evaluate the chemical composition and hydro-chemical characteristics of water content, Schoeller's (1962) diagram (Fig 4.13), and composition (bivariate or scatter diagram) were applied. The composition diagram provides a handy way to visually express large number of data, complements the fingerprint diagram. Piper's (1963) diagram was applied to classify waters of the Basin into different facies and to infer the composition of aquifer materials being tapped

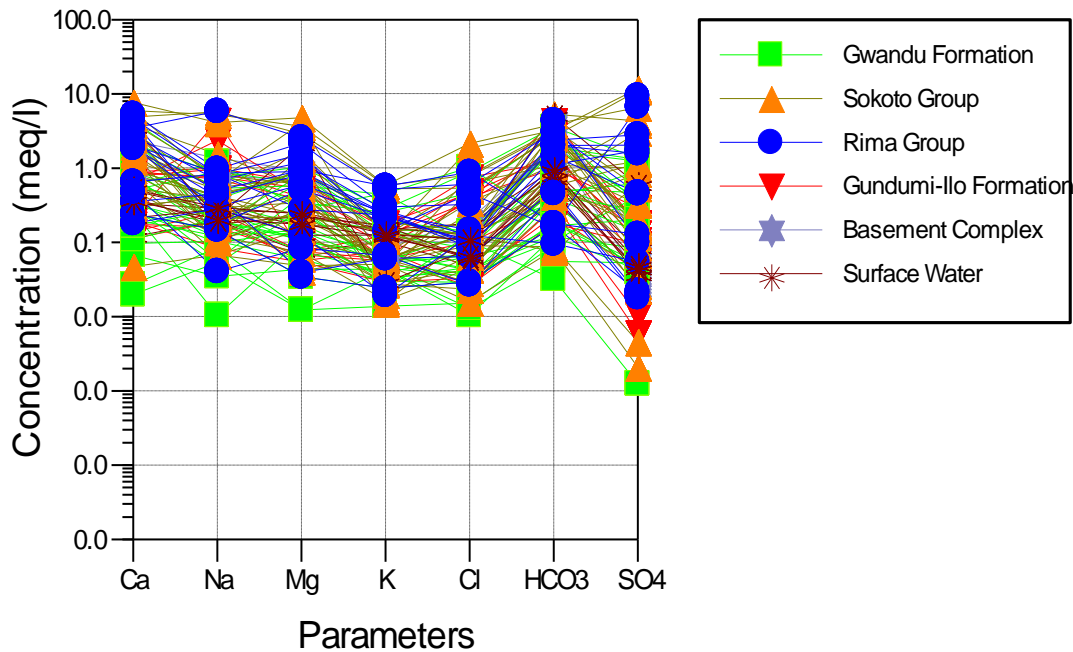


Figure 4.13 Schoeller diagram of sampled waters in the study area

The Schoeller's diagram gives a visual description of the comparative abundance pattern of dissolved ions in each sample and also sorts the hydrochemical data into groups. The compositional variations of all the ions like calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^+), (as in Fig 4.13) are such that it is tasking to pin point which one of them is commonly dominant. Hence, the chemical composition of the waters from various aquifers in the study area was re-presented in subsequent paragraphs in accordance with groundwater from distinct aquifer types and surfacewater from the study area.

4.4.1 Gwandu Formation

In this Formation, Ca-HCO_3 water type was observed to generally describe the groundwater type as it is evidenced with highest mean (0.76meq/L) of calcium ion as dominant cation compare to mean values of other cations ($\text{Mg}^{+2}=0.35\text{meq/L}$, $\text{Na}^+=0.29\text{meq/L}$, $\text{K}^+=0.12\text{meq/L}$)

measured. Similar evidence was observed for the anions, with HCO₃ mean value of 0.9meq/L as dominant anion, over other anions: SO₄ (mean=0.29meq/L) and Cl (mean= 0.15meq/L) (see Table 4.9). Hence, the highest recorded mean for cation (Ca) and the highest recorded mean for anion (HCO₃) were joined to form the water type Ca-HCO₃ (Mazor, 2004).

Table 4.9 Chemical Composition (in meq/l) of water of the Gwandu Formation in Sokoto basin

Stn ID	Location	Sample ID	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄
Units			meq/L	meq/L	meq/L	meq/L	meq/L	meq/L	meq/L
GWSS64	Silame	GW	0.39	0.05	0.08	0.05	0.06	0.32	0.13
GWSS78	Ganbuwa	GW	4.24	1.04	0.76	0.28	0.89	3.56	1.38
GWSS2	Binji	GW	0.1	0.06	0.1	0.03	0.03	0.19	0.05
GWSS3	Gidan Madi	GW	0.59	0.28	1.2	0.46	1.02	0.18	0.05
GWSS4	Tangaza	GW	0.07	0.04	0.03	0.04	0.01	0.12	0.08
GWSS5	Balle	GW	0.33	0.82	0.17	0.13	0.08	1	0.34
GWSS31	Rundi	GW	0.58	0.18	0.33	0.06	0.07	0.38	0.03
GWSS34	Yabo	GW	0.11	0.08	0.21	0.04	0.06	0.12	0.04
GWSS35	Shagari	GW	0.89	0.11	0.19	0.06	0.14	0.34	0.04
GWSS36	Gwandu	GW	0.03	0.01	0.09	0.01	0.02	0.09	0.01
GWSS37	Tambuwal	GW	2.13	0.34	0.86	0.25	0.46	2.9	0.35
GWSS39	Kalgo	GW	0.02	0.01	0.05	0.04	0.01	0.06	0.05
GWSS40	Birnin Kebbi	GW	0.88	0.91	0.38	0.15	0.13	1.95	0.39
GWSS41	Goru	GW	0.17	0.1	0.27	0.07	0.04	0.12	0.08
GWSS44	Alwasa	GW	0.2	0.15	0.12	0.07	0.02	0.4	0.14
GWSS43	Dageri	GW	0.35	0.22	0.12	0.14	0.1	0.03	0
GWSS45	Tungan Isiaka	GW	0.51	0.62	0.91	0.2	0.14	2.25	0
GWSS57	Tambuwal	GW	0.68	0.11	0.2	0.03	0.05	0.59	0.22
GWSS58	Sanyinna	GW	0.77	0.25	0.13	0.05	0.07	0.47	0.63
GWSS59	Tiggi	GW	0.29	0.28	0.05	0.05	0.03	0.42	0.28
GWSS60	Argungu	GW	0.44	0.42	0.06	0.07	0.04	0.52	0.47
GWSS61	Birnin Kebbi	GW	0.95	0.92	0.42	0.2	0.12	1.88	0.35
GWSS62	Kalgo	GW	0.26	0.14	0.1	0.05	0.04	0.1	0.42
GWSS63	katami	GW	0.26	0.11	0.01	0.03	0.04	0.17	0.2
GWSS75	Salah	GW	2.5	1.24	0.12	0.02	0.07	3.4	0.55
GWSS76	Gundun	GW	2.07	0.58	0.54	0.44	0.11	1.92	1.31
Min			0.02	0.01	0.01	0.01	0.01	0.03	0
Max			4.24	1.24	1.2	0.46	1.02	3.56	1.38
Mean			0.76	0.35	0.29	0.12	0.15	0.9	0.29

In the groundwater of Gwandu Formation, the Ca-HCO₃ water type observed characterizes the recharge area of the Formation (Mazor, 2004). Overlying the sandstone bed of Gwandu Formation aquifer is the resistant clay bed capped with ironstone (Anderson and Ogilbee, 1973; Kogbe 1979). Lignite is common to the clay and sand bed (Anderson and Ogilbee, 1973). Groundwater in the recharge area of sandstone aquifers in sedimentary basin is mainly of HCO₃ type which changes to SO₄-Cl type in the direction of flow (Mazor, 2004, Hiscock, 2005 and Singhal and Gupta, 2010). However, the Na-HCO₃ water type also observed in some locations, indicate effect of ion-exchange (Kehew, 2001). This is expected as Gwandu Formation is described by interbedded clay sediment of low permeability (Anderson and Ogilbee, 1973). In view of the above facts, Singhal and Gupta (2010) noted that where rocks are interbedded with shales and other low permeability formations, there may be development of Na-HCO₃ and Na-Cl water due to ion exchange. Na-HCO₃ water type observed occurred at Gwandu locality, Kalgo police station and Goru locations while Ca-SO₄ water type recorded were at Sanyinna Tambuwal, Katami and Salame (Table 4.9) above.

The origin of SO₄²⁻ in recharge area is presumably due to pyrite and/or gypsum dissolution (Hiscock, 2005, Singhal and Gupta, 2010). The decrease in SO₄ in sedimentary basin has been reported in some places. The decrease in SO₄²⁻ appears to be as a result of sulphate reduction in the presence of reduced carbon (lignite) while increase in chloride is attributed to cross flow of saline water from underlying Pierre shale (Thorstenson *et al.* 1979). Leakage from interbedded aquitards (clay, siltstone deposits) causing an increase in Cl⁻ content of groundwater is also reported from the Triassic Sherwood sandstone aquifer in northwest England (Kimblin 1995). Na-Cl water type was also noted to have occurred at station ID: GWSS3 (Gidan Madi). Clay and shales also play an important role in acting as semi-permeable membrane (osmotic filters) in spite of their low permeability believed to be

responsible for the occurrence of saline waters in non-marine sediments (Back and Hanshaw 1965; Neuzil 1986). The average sequence of abundance of ions in the Gwandu Formation is generally presented in Table 4.8 and then expressed as: $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$ and $\text{HCO}_3 > \text{SO}_4 > \text{Cl}$ (meq/L). The variation of the variants (ions compositions) in this Formation that contributed to different water types identified and to the nature of trend observed in Fig. (4.14).

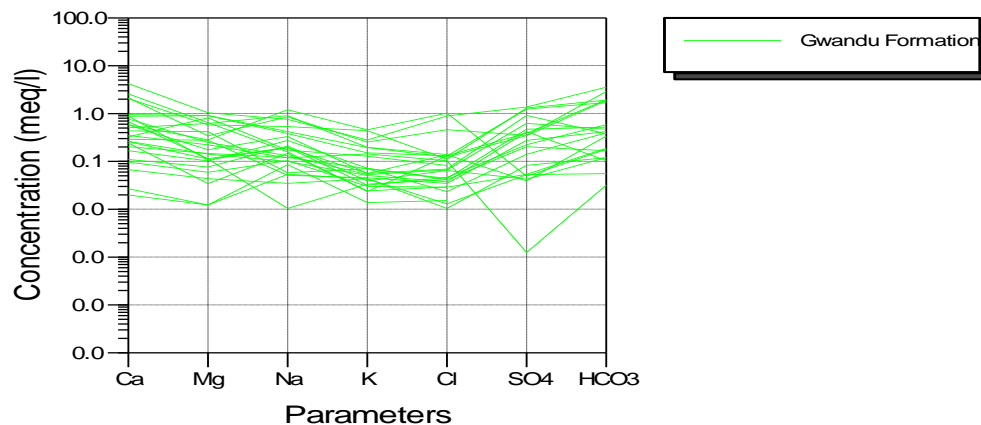


Figure 4.14 Schoeller's diagram of sampled waters from Gwandu Formation

The groundwater chemical composition of Gwandu Formation is such that at near-surface the groundwaters are diluted and are of Ca-Na-HCO₃ type as observed at stations Rundi, Shagari, Tambuwal, Kangiwa, Tambuwal and Silame, (Table 4.8) similar observation was reported by Hiscock, (2005). With increased depth (Singhal and Gupta, 2010) the groundwater becomes brackish and tends towards Na-Ca-HCO₃ type as observed in stations ID like GWSS 36 (Gwandu locality) and GWSS 41 (Goru). In the Gwandu Formation, the change from Ca-Na-HCO₃ to Na-Ca-HCO₃ water type with increased depth can be explained by cation exchange (for Na) on clay minerals of the Formation (Gascoyne and Kamineni, 1993).

The results of the Gwandu Formation water isotope composition in the study area are presented in Figure 4.15 and discussed with respect to the Global Meteoric Water Line (GMWL).

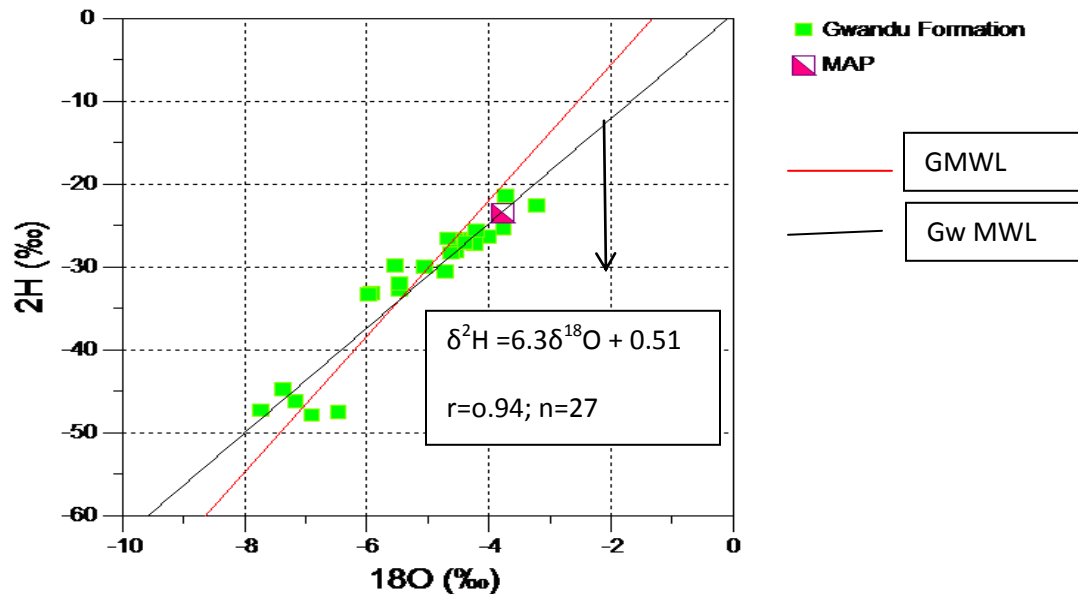


Fig 4.15 $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ plot of the investigated groundwaters from Gwandu Formation aquifer

Gwandu Formation ground water samples show $\delta^{18}\text{O}$ values between -7.72 and -3.2‰, and $\delta^2\text{D}$ values between 47.9‰ and -21.5‰. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ data points of the groundwater samples cluster around the GMWL (Fig. 4.13), suggesting a meteoric recharge, derived from rainfall which rapidly recharges the Gwandu Formation aquifer through the weathered overburden and ingresses such as joints and fracture systems. Also, Figure 4.15 shows that the groundwater samples are distributed around the Gwandu meteoric waterline (Gw MWL), and indicates no significant isotopic modifications by evaporation, which means that the recharge of the aquifer is quite rapid and the recharging meteoric water does not occupy the soil zone of the recharge area for a long time, (Fehdi *et al.*, 2011). Moreover, samples do not show any tendency towards standard isotopic sea water values (0.0‰, 0.0‰; Fig. 4.15) which conforms with Carol *et al.* (2009) findings. Two water types were clearly visible from the Fig. 4.15, the

depleted waters in stable isotopes of $\delta^{18}\text{O}$ ranging from -7.72‰ to -6.46‰ and of $\delta^2\text{H}$ from -47.92‰ to -44.85‰ and modern waters of $\delta^{18}\text{O}$ ranging from -6.0‰ to -3.5‰ and $\delta^2\text{H}$ from -33.42‰ to -21.49‰. The depleted waters depict evidence of paleoclimate effect on Gwandu Formation (Kebede, 2012). He rightly stated that the paleoclimatic effect in arid regions is manifested by depletion in stable isotopes with respect to modern waters. GwMWL was observed from the overall groundwater data from Gwandu Formation using the least-square-fit linear regression (Celle-Jeonathan *et al.*, 2001) between $\delta^{18}\text{O}$ and $\delta^2\text{H}$. The expression below GwMWL characterised Gwandu Formation.

$$\delta\text{D} = 6.3\delta^{18}\text{O} + 0.51; r = 0.94; n = 27$$

where r denote the correlation factor and n the sample size. From the expression, the GwMWLs' slope of 6.3 and low deuterium excess value of 0.51 was obtained. This slope realized is low compare to global standard slope value of 8 and deuterium excess value of 10‰ (Craig, 1961a). The decrease in d-excess value may be attributed to the evaporation of falling raindrops (Al-Gamal, 2011). The low d-excess (≤ 6) values obtained from GwMWL in the study area indicate that there is evaporation of recharge water, leaving the residual groundwater with lower values of d-excess, (Hoefs, 2009; Al-Gamal, 2011). The decrease in slope value relative to standard value may suggest that infiltrating rainwater were enriched in heavy isotopes prior to recharge (Carol *et al* 2012; Carucci *et al.*, 2012; Yidana, 2013).

4.4.2 Sokoto Group

The general water type observed in this Formation is Ca-SO_4 type (see Fig. 4.16). This reflects the presence of gypsum aquiferous material. Other water types (Ca-HCO_3 , Na-HCO_3) identified is well represented in the trend of ion distribution observed in Fig. 4.16.

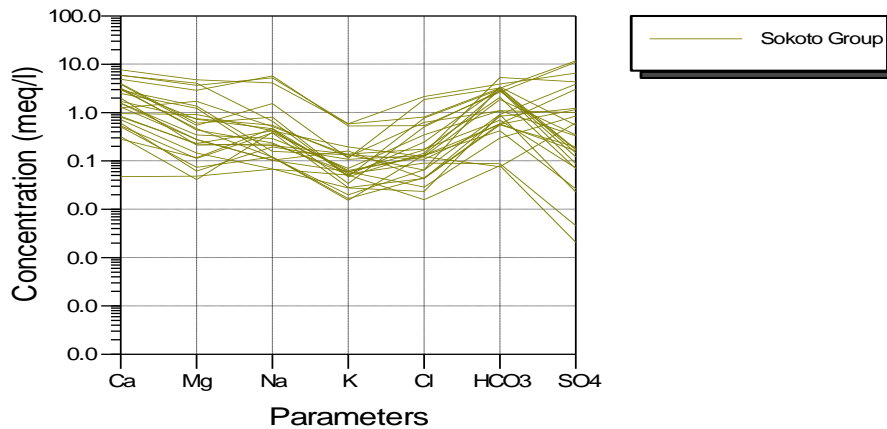


Figure 4.16 Schoellers' diagram of groundwater from Sokoto Group in the study area

The Ca-HCO₃ water type noted to be peculiar to these stations: GWSS6, GWSS21, GWSS30, GWSS47, GWSS48, GWSS53, GWSS54, GWSS65, GWSS66, GWSS77, GWSS84, GWSS52, GWSS73, GWSS51, and GWSS85 (as shown in Table 4.10) may be attributed to the occasional limestone aquifer materials in the lower part of the Group (Dange Formation) reported by Anderson and Ogilbee (1973). Besides, the Ca-HCO₃ water type observed in the aquifer reflects presence of Carbonate rocks or Carbonate aquifers (Mazor, 2004, Hiscock, 2005 and Singhal and Gupta, 2010). Singhal and Gupta (2010) stated that groundwater in carbonate rocks contains more alkaline earths and carbonate ions relative to alkalis, chloride and sulphate. Both Ca-Mg and Na-rich waters was identified in this Group. As such, the ground water composition of Sokoto Group varies mainly between Ca-SO₄, Ca-HCO₃ and Na-HCO₃ type. Na-HCO₃ water type was noted to occur at stations ID: GWSS17 and GWSS70 (see Table 4.10).

Table 4.10 Chemical Compositions of waters of the Sokoto Group aquifer in the Sokoto basin (meq/l)

Stn.ID	Location	Ca meq/L	Mg meq/L	Na meq/L	K meq/L	Cl meq/L	HCO ₃ meq/L	SO ₄ meq/L
GWSS83	Chacho	1.57	0.28	0.1	0.16	0.04	0.84	1.23
GWSS84	Skt Town1	3.15	0.73	0.46	0.03	0.51	2.82	0.17
GWSS85	Skt Town 2	4	0.61	0.81	0.05	0.77	3.04	0.12
GWSS81	Shuni	1.3	0.28	0.1	0.12	0.03	0.58	1.15
GWSS6	Gwadabawa	5.9	4.07	0.67	0.05	0.14	5.36	4.35
GWSS7	Mammasuka	1.71	0.75	0.55	0.12	0.63	1.1	0.33
GWSS17	Tsamaye	0.28	0.12	0.47	0.05	0.09	0.09	0
GWSS21	Marnona	0.85	0.22	0.21	0.14	0.18	0.7	0.07
GWSS29	Wammakko	2.92	1.37	0.16	0.13	0.06	0.92	3.89
GWSS30	Kalambaina Pri.Sch	3.87	0.54	1.55	0.11	1.87	3.24	0.15
GWSS32	Bodinga	0.81	0.23	0.42	0.06	0.03	0.3	0.85
GWSS33	Lambar Marzuru	0.05	0.05	0.07	0.05	0.02	0.08	0
GWSS47	Skt.FGC	3.2	0.44	0.24	0.05	0.25	3.28	0.18
GWSS48	Sabongari.Skt	1.57	0.35	0.29	0.07	0.35	1.1	1.01
GWSS51	Sifawa	0.53	0.11	0.38	0.03	0.04	0.56	0.19
GWSS52	Jabo	0.61	0.06	0.2	0.11	0.13	0.42	0.03
GWSS53	Dogongaji	2	0.21	0.22	0.06	0.17	2.08	0.07
GWSS54	Barkeji	0.71	0.15	0.07	0.03	0.02	0.91	0.02
GWSS65	Tulluwa	3.03	0.47	0.12	0.02	0.13	2.98	0.09
GWSS82	Rabah	0.32	0.04	0.39	0.06	0.12	0.08	0.61
GWSS67	Gigane	7.69	4.8	4.13	0.59	2.16	3.92	6.57
GWSS68	Illela	1.26	1.72	0.51	0.13	0.11	0.59	3.05
GWSS69	Gidan Cwake	5.96	3.68	5.26	0.59	0.81	3.22	11.83
GWSS70	Wauru	4.89	2.9	5.75	0.53	0.54	2.66	11.09
GWSS71	Rafin Duma	13.45	9.44	2.6	0.54	0.42	0	28.69
GWSS73	Rugar Kijo	0.55	0.07	0.12	0.02	0.04	0.58	0.16
GWSS75	Salah	2.5	1.24	0.12	0.02	0.07	3.4	0.55
Min		0.05	0.04	0.07	0.02	0.02	0	0
Max		13.45	9.44	5.75	0.59	2.16	5.36	28.69
Mean		2.77	1.29	0.96	0.15	0.36	1.66	2.83

Results of stable isotopic composition survey of Sokoto Group are presented in Fig. 4.17. Two main water types were identified however a groundwater sample from this group tend to be an evaporated water type as shown in the Fig. 4.17.

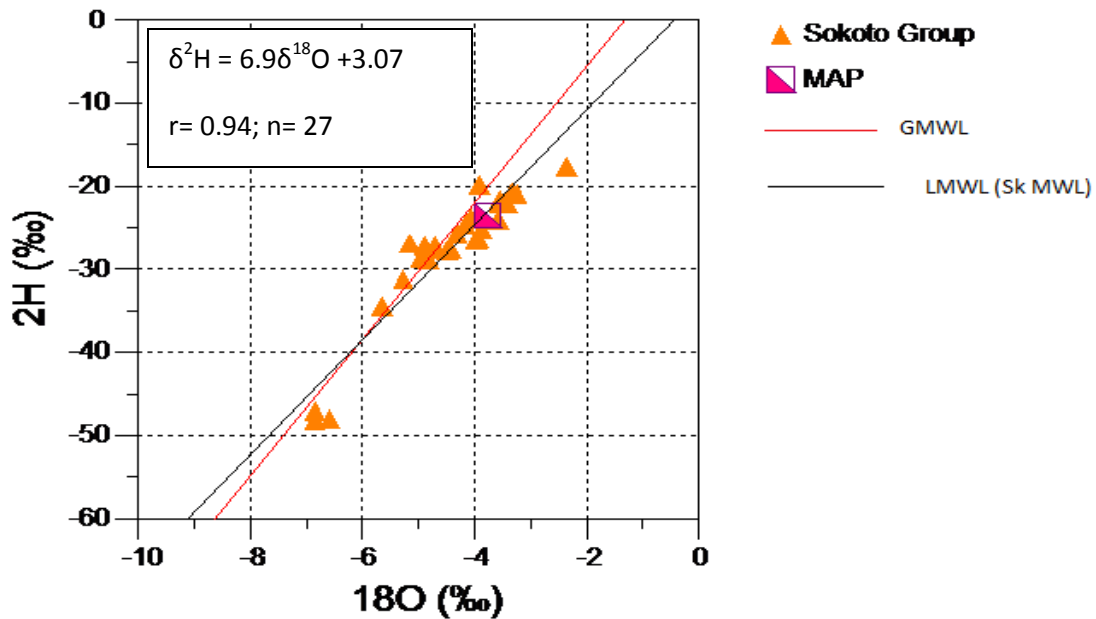


Figure 4.17 $\delta^2\text{H}$ vs. $\delta^{18}\text{O}$ plot of the investigated groundwaters from Sokoto Group aquifer

The isotope composition of groundwaters in Sokoto Group is depicted by their $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values ranging from -48.2‰ to -17.65‰ and -6.85‰ to -2.36‰ respectively. Also, in Fig. 4.17, a local meteoric line of Sokoto Group (Sk MWL) is obtained: $\delta^2\text{H} = 6.9\delta^{18}\text{O} + 3.07$. The Sk MWL(s) has low slope (6.9) and deuterium excess (3.07) than the GMWL (Craig, 1961), and is thus indicative of the effects of high evaporation rates attributable to high temperatures, and low relative humidity in arid region (Mazor, 2004; Yidana, 2013). Adomako *et al.*, (2011) reported that low d-excess indicates infiltrated rain-water might have undergone some degree of fractionation both on land surface and in the unsaturated (vadose) zone, before entering the groundwater reservoir.

More so, the stable isotope values of groundwater in this Group tend to scatter along the meteoric lines but reveal an internal order such that values of deeper groundwaters are isotopically lighter (more negative) than shallow groundwaters and evaporated groundwater.

4.4.3 Rima Group

This Group consists of marly limestone, shale and gypsum among the sediment compositions (Anderson and Ogilbee, 1973). So, the main water type recorded in this group is Ca-SO₄ type (see Fig.4.18). However, other water types noted in few locations in the Group are: Ca-Cl, was noted in GWSS55; Ca-HCO₃ water type was observed in stations GWSS56, GWSS74, GWSS1 and GWSS25; Na-HCO₃ was clearly shown by groundwater sampled stations 18 and 20 and Na-SO₄ water types was recorded at GWSS19. These water types identified were attributed to the dissolution of aquifer constituents and cation-exchange effects. As such were the contributing factors for the varied trend observed in the finger plot in Fig (4.18).

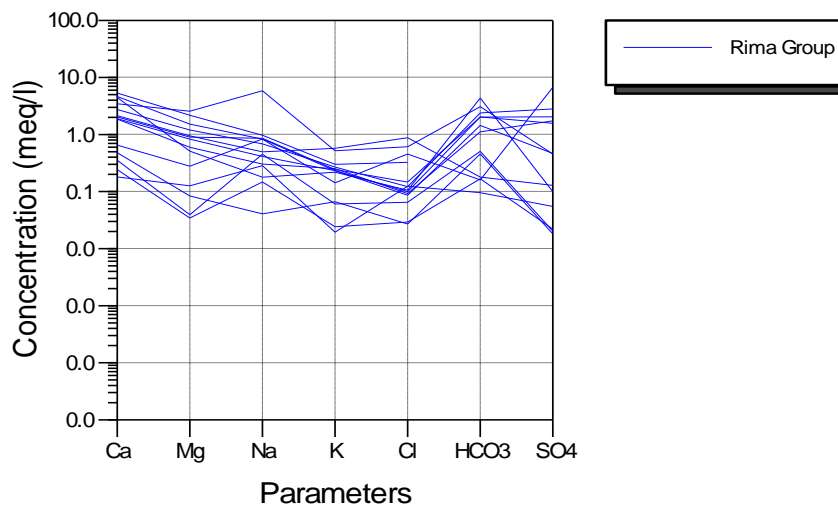


Figure 4.18 Schoellers' diagram of assesses groundwater from Rima Group aquifer

In view of the above, Mazor(2004), stated that the sediments constituents (such as Marly limestone, shale and Gypsum) in this Group are characterized by the associated lithological imprints, such that, Marl rock is characterized by HCO₃⁻ and Cl⁻ as major anions, Na⁺ and Ca⁺² as major cations; Limestone by HCO₃⁻ as major anion, and Ca⁺² as dominant cation and Clay and shale often containing rock salt and gypsum characterized by Cl⁻ as dominant anion,

followed by SO_4^{-2} ; and Na^+ as major cation while Gypsums by SO_4^{-2} as dominant anion and Ca^{+2} as dominant cation, followed by Mg^{+2} or Na^+ . The general average ions order of occurrence in the Rima Group realized from this study is presented as follows:

Rima Group: $\text{Ca} > \text{Na} > \text{Mg} > \text{K}$ and $\text{SO}_4 > \text{HCO}_3 > \text{Cl}$ (meq/L) (See Table 4.11).

Table 4.11 Chemical Composition of waters of the Rima Group aquifer in the Sokoto Basin (meq/l)

Stn ID	Location	Sample.ID	Ca	Mg	Na	K	Cl	HCO_3	SO_4
Unit		Unit	meq/L	meq/L	meq/L	meq/L	meq/L	meq/L	meq/L
GWSS19	Taloka	WU	3.47	2.56	5.86	0.52	0.61	3.08	8.93
GWSS20	Goronyo Town	WU	0.65	0.28	0.84	0.23	0.09	1.45	0.47
GWSS1	Kware	WU	4.47	0.51	0.18	0.22	0.11	4.36	0.1
GWSS74	Bancho	WU	0.24	0.03	0.15	0.02	0.03	0.17	0.02
GWSS79	Yabo	WU	0.18	0.13	0.29	0.02	0.12	0.1	0.06
GWSS72	Gada	WU	4.66	1.52	0.83	0.14	0.46	0.16	6.75
GWSS22	Wurno	WU	1.87	0.6	0.3	0.25	0.09	1.12	1.75
GWSS23	Kofar Rima. Wu	WU	2.04	0.9	0.86	0.24	0.15	2.02	2.04
GWSS24	Kanwuru. Wu	WU	5.35	2.18	0.97	0.3	0.33	0	9.39
GWSS25	Kandam	WU	1.9	0.83	0.41	0.23	0.1	2.04	1.58
GWSS26	Hamma-Ali	WU	2.75	1.21	0.69	0.27	0.12	2.4	2.82
GWSS55	Kebbe	WU	2.14	0.95	0.5	0.57	0.88	0.18	0.13
GWSS56	Romom Sarki	WU	0.48	0.08	0.04	0.07	0.03	0.46	0.02
GWSS8	Tumbulla	WU	0.35	0.04	0.45	0.06	0.07	0.51	0.02
Min			0.18	0.03	0.04	0.02	0.03	0.01	0.02
Max			5.35	2.56	5.86	0.57	0.88	4.36	9.39
Mean			2.18	0.84	0.88	0.22	0.23	1.29	2.43

All $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of ground water samples from Rima Group part of the study area are plotted in Fig.4.19 on a $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ diagram. Rima Group meteoric water line (Rm MWL) obtained is given in the equation:

$$\delta^2\text{H} = 7.46\delta^{18}\text{O} + 4.5, \text{ with correlation factor, } r = 0.96 \text{ and sample size, } n = 14.$$

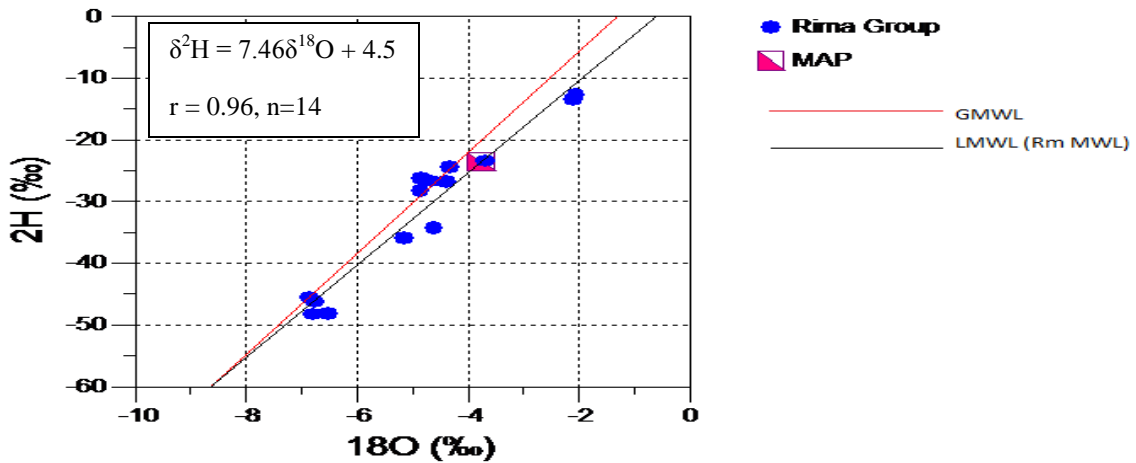


Fig. 4.19 $\delta^{18}\text{O}$ vs. $\delta^2\text{H}$ correlation for groundwaters from Rima Group in the study area

It was characterized by a different local meteoric line compare to other Formations in the Basin of the study area. Also, it can be deduced from Fig. 4.19 that the groundwaters of this Group are of meteoric origin with low slope and low d-excess value compare to GMWL (Craig, 1961a). The ground water samples in the Rima Group were binned into three isotopic sub-groups as shown in Fig. 4.19. They include depleted waters (more negative), moderately depleted waters and evaporated water.

The depleted waters group consisted of four bicarbonates and sulphate waters (GWSS26, GWSS25, GWSS23, and GWSS20) where ground water exhibited the most negative $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values. These $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values ranged from -48.31‰ to -45.56‰ and -6.86‰ to -6.51‰ respectively. The moderately depleted waters grouping consisted of 8 sampled waters (GWSS24, GWSS22, GWSS73, GWSS74, GWSS79, GWSS56, GWSS55, GWSS55 and GWSS1). Ground water in this group had $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values that were more positive than the depleted waters group, and ranged from -36.00‰ to -23.44‰ and -5.15‰ to -3.69‰ respectively. The evaporated groundwaters group consisted of 2 mainly sulphate waters

from wells samples identity (ID) GWSS 19 and GWSS72. Ground water in the third group had more positive $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values than the other ground waters that ranged from -13.52 ‰ to -12.75‰ and -2.11 ‰ to -2.05‰ respectively. Groundwaters exhibiting more negative $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values may be indicative of wells that intersected deep fractures recharged with old ground water from colder climatic conditions with little mixing of older ground water with young ground water. Groundwaters with more positive $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values could be a result of wells that intersected fractures recharged with younger ground water (Wassenaar *et al*, 2011). Besides, silicate mineral weathering in aquifers does not appreciably affect $\delta^{18}\text{O}$ signatures (Clayton *et al.*, 1966; Drever, 1988).

4.4.4 Gundumi-Ilo Formation

Two obvious water types observed in this Formation are Na-HCO₃ and Ca-HCO₃ as presented in Fig 4.20.

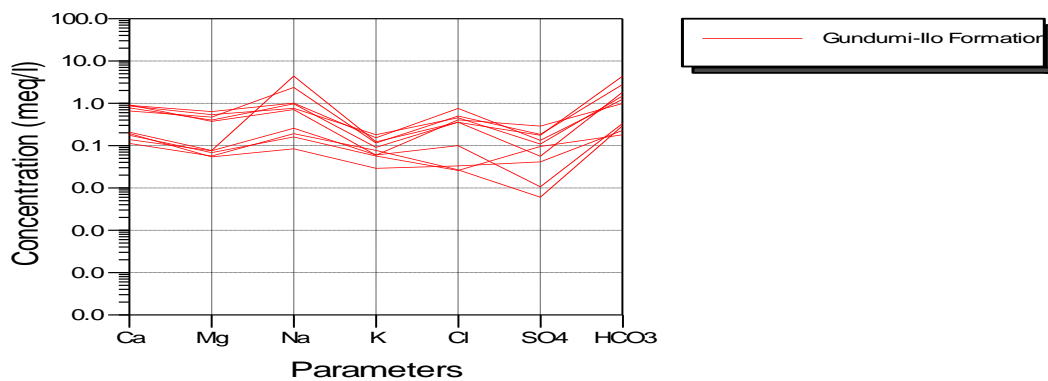


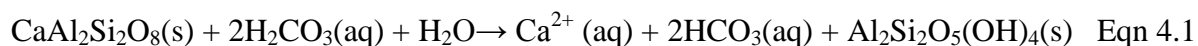
Figure 4.20 Schoellers' diagram of sampled groundwaters from Gundumi-Ilo Formation in the study area.

Generally, average ions order of occurrence in the Formation is presented as Ca>Mg>Na>K and HCO₃>SO₄>Cl (meq/L) in Table 4.12.

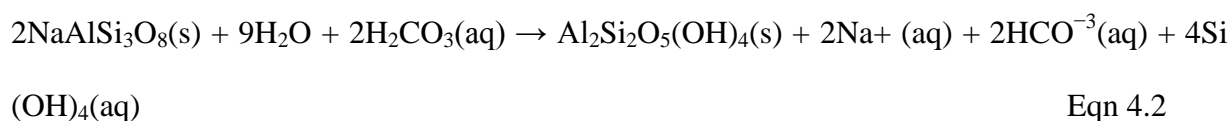
Table 4.12 Chemical Composition of the waters of Gundumi-Ilo Formation aquifer (meq/l)

Station ID	Location	Sample ID/ Unit	Ca meq/L	Mg meq/L	Na meq/L	K meq/L	Cl meq/L	HCO ₃ meq/L	SO ₄ meq/L
GWSS9	Gundumi	GU	0.14	0.08	0.26	0.06	0.1	0.33	0.01
GWSS87	YarGeda	GU	0.91	0.37	0.71	0.06	0.41	0.99	0.29
GWSS86	Bimasa	GU	0.19	0.05	0.08	0.03	0.03	0.23	0.04
GWSS10	Gidan sale	GU	0.11	0.06	0.19	0.08	0.03	0.29	0.01
GWSS11	Shinkafi 1	GU	0.78	0.4	0.97	0.09	0.36	1.82	0.06
GWSS12	Shinkafi 2	GU	0.66	0.47	2.38	0.12	0.5	2.78	0.18
GWSS13	Isa	GU	0.89	0.64	1.01	0.15	0.76	1.24	0.13
GWSS14	Tarshar Bagaruwa	GU	0.21	0.08	4.4	0.12	0.36	4.36	0.18
GWSS16	Sabon Birnin	GU	0.87	0.54	0.76	0.18	0.46	1.48	0.11
GWSS38	Karama D.Cunity	GU	0.18	0.07	0.16	0.06	0.03	0.18	0.1
Min			0.11	0.05	0.08	0.03	0.03	0.18	0.01
Max			0.91	0.64	4.4	0.18	0.76	4.36	0.29
Mean			0.49	0.28	1.09	0.1	0.3	1.37	0.11

The two water types observed in this Formation may be attributed to the weathering of lithological imprints associated with this Formation. It consist of quartz and feldspar pebble gravel interbedded with the abundant clay and clayey sand, sandy bed as well as a conglomerate of rounded quartz pebbelsand feldspathic and micaceous materials especially of bed constituent, (Anderson and Ogilbee, 1973; Kogbe, 1979). Weathering processes participate in controlling the hydrogeochemical cycles of many elements, (Hiscock, 2005). The two following reactions (se equs 4.1 and 4.2) provide examples of important silicate weathering processes. Firstly, taking Ca-rich plagioclase feldspar (anorthite) the incongruent weathering reaction resulting in the aluminosilicate residue kaolinite is written (Andrews *et al.* 2004):



In this weathering reaction, H⁺ ions dissociated from H₂CO₃ hydrate, the silicate surface and naturally buffer the infiltrating groundwater such that the ionic bonds between Ca²⁺ and the SiO₄ tetrahedral are easily broken, releasing Ca²⁺ into solution resulting in a Ca-HCO₃ water type. Secondly, for the Na-rich plagioclase feldspar (albeit) the incongruent reaction producing kaolinite and releasing Na⁺ and HCO₃⁻ ions is presented as:



In most cases, Mazor (2004) stated that water containing HCO₃⁻ indicates CO₂-induced interactions with rocks, and the balancing cations indicate the types of rocks passed.

Isotope composition of Gundumi-Ilo Formation is such that the stable isotopes of δ²H and δ¹⁸O ranged between -51.4‰ to -14.84‰ and -7.28‰ to 2.47‰ respectively. Presented in Fig. 4.21 is the isotopic composition of groundwater sampled from wells from Gundumi-Ilo Formation.

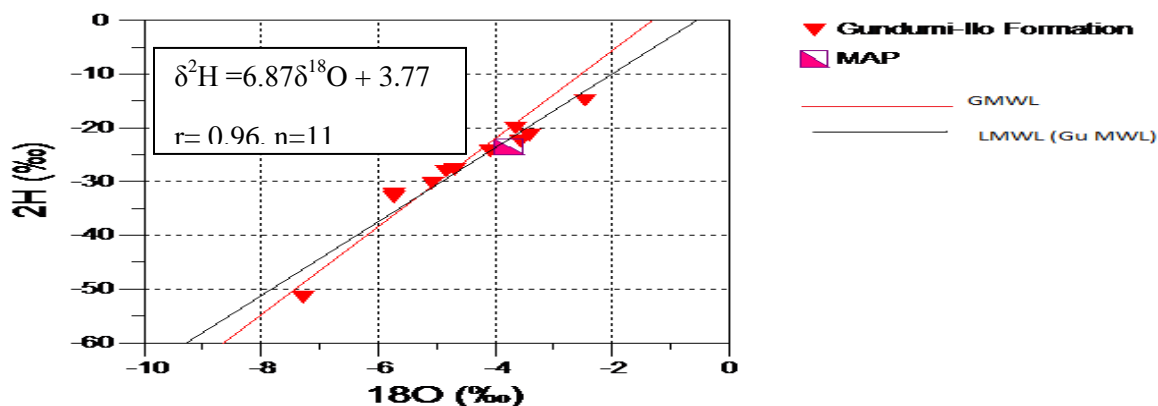


Figure 4.21 Isotope composition of groundwaters sampled from wells from Gundumi-Ilo Formation of the study area.

Clearly, Fig. 4.21 shows depleted, moderately depleted and evaporated water. The more negative isotope data (depleted) of the groundwater samples relative to the rain sample in the area can be attributed to climatic and seasonal differences (Dansgaard, 1964; Loh *et al.*, 2012).

The low slope (6.87) and characteristics d-excess (3.77‰) observed in (Fig. 4.21) may suggest that infiltrating rainwater were enriched in heavy isotopes prior to recharge and during the process of infiltration and percolation through the unsaturated zone to the saturated zone, (Yidana, 2013).

4.4.5 Surface water

The general water type for the surface waters of Sokoto Basin is Ca-HCO₃ type (Fig. 4.22).

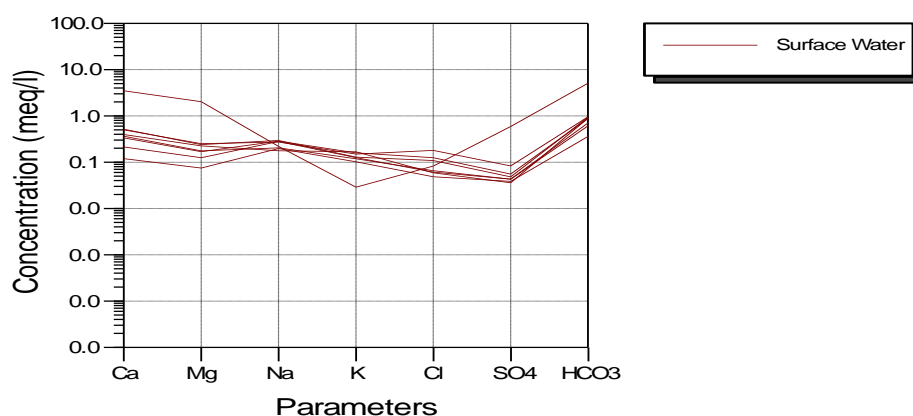


Figure 4.22 Schoellers' diagram of surface waters sampled from the study area.

Differences in composition of major ions and their concentrations in the surface waters of Sokoto basin reflect the complex geological structure of the region and probably introduction of contaminants into surfacewater from human activities (Sutcliffe *et al.* 1982; Hiscock, 2005).

These impart varying amounts of sodium, potassium, calcium, magnesium, bicarbonate and sulphate ions to surface waters after contact with soil, groundwater and, especially, the underlying rocks through three main routes (Tipping 1990, 1996).

- i. During periods of high rainfall, surface runoff directly enters watercourses, thereby temporarily diluting the concentrations of some ions in streams and surface waters of dams and lakes, whilst the concentration of hydrogen and dissolved ions are raised.

- ii. Water percolates into the soil, consisting of an upper an upper organic horizon and lower mineral horizon and moves laterally downhill into the nearest stream.
- iii. Water percolates down through the soil horizons and makes contact with the underlying bedrocks in the unsaturated zone, before finally entering a stream and
- iv. Deep ground water held in rocks and rising to the surface in some localities (Sutcliffe *et al.* 1982). The deviations of the surface water samples from the GMWL (Fig. 4.23) are a result of evaporative enrichment of the heavier isotopes.

The average order of occurrence is thus presented as $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$ and $\text{HCO}_3 > \text{SO}_4 > \text{Cl}$ (meq/L) (Table 4.13).

Table 4.13 Chemical Composition of the Surface Water in the Sokoto Basin (meq/l)

Station ID	Location	Ca meq/L	Mg meq/L	Na meq/L	K meq/L	Cl meq/L	HCO ₃ meq/L	SO ₄ meq/L
SRES80	Shagari Dam	0.4	0.23	0.18	0.17	0.06	0.89	0.04
SRI66	Balkori Bridge	3.5	2.03	0.22	0.03	0.08	5.08	0.59
SRES18	Goronyo Dam	0.21	0.13	0.28	0.13	0.06	0.61	0.04
SRES15	Rima river	0.12	0.07	0.2	0.1	0.05	0.36	0.04
SRIS42	Rima River	0.5	0.25	0.27	0.15	0.18	0.96	0.08
SRIS27	Rima River	0.52	0.24	0.3	0.13	0.11	0.94	0.05
SRIS28	Sokoto River	0.36	0.18	0.2	0.12	0.07	0.7	0.04
SRIS46	Argungu...	0.34	0.17	0.29	0.16	0.12	0.88	0.06
Min		0.12	0.07	0.18	0.03	0.05	0.36	0.04
Max		3.5	2.03	0.3	0.17	0.18	5.08	0.59
Mean		0.74	0.41	0.24	0.12	0.09	1.3	0.12

Fig. 4.23 shows that the most enriched waters in isotope signature in the basin comprises mainly of surface waters due to exposure of water to vapor loss and probably, evaporation of rain droplets.

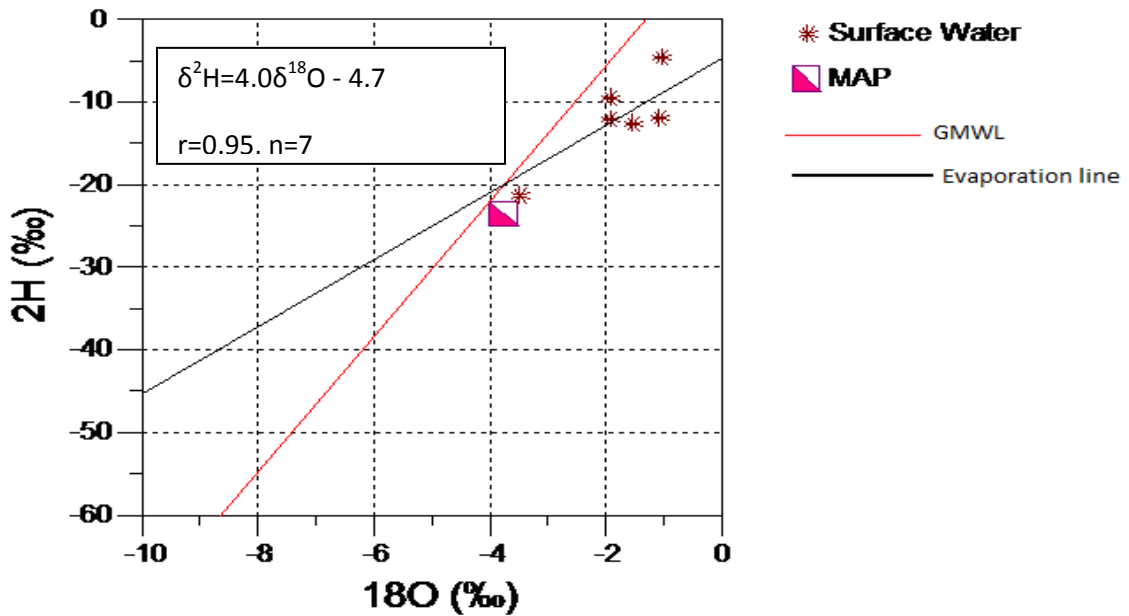


Figure 4.23 Isotope composition of water sampled from surfacewater in the study area

This explains why the residual waters tend to deviate from the global world meteoric line (GMWL), with evaporation slope of 4.0 (Fig. 4.23). The slope observed is within standard evaporation line that varies between 4.0 and 5.0 (Kebebe, 2012). The slope and intercept observed are not far from results obtained elsewhere, (Yidana, 2013). The data fall on an evaporation line defined by Equation embedded in Fig 4.23 whose slope is lower than that of the GMWL. This observation is attributed to evaporative enrichment of the heavier isotopes of both Hydrogen and Oxygen. Evaporation of surface water bodies causes enrichment in the heavier isotopes of the residual water.

4.4.6 General Characterization of the Waters of the Basin by Hydrochemical Approach

Meticulous examination of Schoellers' plots generally showed variation in ions composition of the waters of the various aquifers in the basin. These variations observed may be due to difference in composition of aquifer materials brought about by weathering reactions, climate conditions or cation exchange (Trainer, 1998; Mazor, 2004; Hiscock, 2005 and Singhal and Gupta, 2010). Potassium ion concentrations were noted to be generally low and the waters in the area with respect to the fingerprint diagram were categorized into bicarbonate and Sulphate water type. The low concentration of the K^+ in the water is probably influenced by reverse cation exchange activity with Ca^{2+} , (Loh *et al.*, 2012).

Furthermore, in the basin the dominant ions with their corresponding relative abundance of cations and anions, observed as presented in the Schoellers' diagrams for the distinct aquifer types and surface water determined were as follows: Surface water: $Ca-HCO_3; Ca > Mg > Na > K$ and $HCO_3 > SO_4 > Cl$ (meq/L), Gwandu Formation; $Ca-HCO_3; Ca > Mg > Na > K$ and $HCO_3 > SO_4 > Cl$ (meq/L), Sokoto Group; $Ca-SO_4; Ca > Mg > Na > K$ and $SO_4 > HCO_3 > Cl$ (meq/L) Rima Group; $Ca-SO_4; Ca > Na > Mg > K$ and $SO_4 > HCO_3 > Cl$ (meq/L) Gundumi-Ilo Formation; $Ca-HCO_3; Ca > Mg > Na > K$ and $HCO_3 > SO_4 > Cl$ (meq/L), and Basement Complex: $Na-HCO_3; Na > Ca > Mg > K$ and $HCO_3 > SO_4 > Cl$ (meq/L). These deductions were based on (Mazor, 2004) conclusion that a more detailed description of water composition includes the relative abundance of cations and anions. The order of ions concentration (See Table 4.14) in the basin were expressed generally as follows: $Ca > Mg > Na > K$ and $SO_4 > HCO_3 > Cl$ (in equivalents per volume of water (meq/L)). Presented in Appendix XIII is the chemical composition of the waters from the sampled locations in the Sokoto Basin.

Table 4.14 Representative chemical composition of the waters in the Sokoto Basin

Station ID	Location	Sample ID/ Unit	Ca meq/L	Mg meq/L	Na meq/L	K meq/L	Cl meq/L	HCO ₃ meq/L	SO ₄ meq/L
SRES15	Rima river	GU	0.12	0.07	0.20	0.10	0.05	0.36	0.04
SRIS28	Skt river	WU	0.36	0.18	0.20	0.12	0.07	0.70	0.04
GWSS49	Kuka Mairafu	BA	2.32	0.93	1.36	0.11	0.10	4.60	0.12
GWSS50	Gidan Gado	BA	0.69	0.70	0.78	0.08	0.20	1.98	0.04
GWSS9	Gundumi	GU	0.14	0.08	0.26	0.06	0.10	0.33	0.01
GWSS87	YarGeda	GU	0.91	0.37	0.71	0.06	0.41	0.99	0.29
GWSS86	Bimasa	GU	0.19	0.05	0.08	0.03	0.03	0.23	0.04
GWSS5	Balle	GW	0.33	0.82	0.17	0.13	0.08	1.00	0.34
GWSS31	Rundi	GW	0.58	0.18	0.33	0.06	0.07	0.38	0.03
GWSS81	Shuni	KA	1.30	0.28	0.10	0.12	0.03	0.58	1.15
GWSS82	Rabah	KA	0.32	0.04	0.39	0.06	0.12	0.08	0.61
Mean			1.60	0.73	0.70	0.14	0.24	1.35	1.38
Min			0.02	0.01	0.01	0.01	0.01	0.00	0.00
Max			13.45	9.44	5.86	0.59	2.16	5.36	28.69

Three distinguished water type (or chemical composition) with corresponding three distinct order of occurrence of cations and anions in the waters of the basin was observed in this study and presented as:

- i. Group1: Ca-HCO₃; Ca>Mg>Na>K and HCO₃>SO₄>Cl (meq/L)
- ii. Group2: Ca-SO₄;Ca>Na>Mg>K and SO₄>HCO₃>Cl (meq/L),
- iii. Group3: Na-HCO₃; Na>Ca>Mg>K and HCO₃>SO₄>Cl (meq/L)

Ca-HCO₃ occurrence in the aquifer partly reflects shallow, fresh ground waters in recharge areas; similarly, Na-HCO₃ reflect shallower portions of confined aquifers and waters deduced here, appear to have been affected by ion exchange (where sodium replaces calcium as the positive ion) (Anderson and Ogilbee, 1973; Loh *et al.*, 2012 and others) and Ca-SO₄ indicates presence of gypsum-bearing sedimentary aquifers and ground waters possibly affected by oxidation of pyrite and other sulfide minerals. The Ca-HCO₃ noted in the study area was attributed to carbonate rock source, Ca-SO₄ observed reflect presence of evaporite (Gypsum)

and Na-HCO_3 to cation- exchange process. These observations are in line with Anderson and Ogilbee, (1973) findings that near the intake areas of all three principal artesian aquifers, the dominant ions are calcium and bicarbonate but, as the water moves down dip, sodium replaces calcium as the positive ion. Also, it conforms with Adelana *et al.* (2003) findings that the characteristic hydrochemical classification in the study area is calcium-alkali-bicarbonate.

Weathering of different rock types, cation exchange and anthropogenic inputs may have contributed to changes in water chemical composition. The main sources of anthropogenic contamination in the area include bush burning, cooking with wood and dung, electric power generators, and vehicular emissions, (AzTech, 2010) Nigeria cement factory, Abattoir, disposal sites among others (Anderson and Ogilbee, 1973), gold mining, limestone mining, tannery, local aluminum utensil production. AzTech's (2010), air quality analysis within the study area reported that the range of levels for the gaseous contaminants measured fall within the National Ambient Air Quality Standards (NAAQS). Given that no anthropogenic emission has been reported from the Sokoto basin (AzTech. 2010), it is assumed that high dissolved ions (Ca^{2+} , Na^+ , Mg^{2+} , K^+ , HCO_3 , SO_4 , Cl , NO_3) in groundwaters came from water rock interaction, anthropogenic input (agriculture; Industry; indiscriminate siting of dumpsite) and cation exchange process. According to Mazor (2004), the lithological parameter is only one of several parameters that control groundwater quality. Factors such as evaporation at the surface prior to infiltration, transpiration, also contribute to water change.

Group I may be waters of carbonate rock origin that could be limestone or dolomite rock. Group II may be waters that have passed through ion-exchange. Group III could be from Evaporites (Gypsum or salt rock). Since salt rock sparingly exists, the Ca-SO_4 identified was therefore attributed mainly to gypsum which is one of the rock types observed in the basin by

previous researcher, (Parker *et al.*, 1964; Anderson and Ogilbee, 1973; Kogbe, 1979; Alagbe, 2004).

More so, the Piper (1944) tri-linear diagram, which is used extensively by various researchers (Ryu *et al.*, 2007; Nti, 2005; Carol *et al.*, 2009; Carucci *et al.*, 2012; Maheshwari *et al.*, (2011); Ji, 2015; and others) in water characterization, was improved by Piper (1953), was applied in this study for the classification of water samples into various facies depending on the relative concentrations of major cations and anions, (Fig. 4.24).

KEY

- A=Ca + Mg-HCO₃
- B=Ca +Mg-HCO₃-SO₄
- C= Ca + Mg-SO₄
- D= Ca + Mg, Na + K-HCO₃
- E=Ca +Mg, Na+K-SO₄
- F=Na + K-HCO₃
- G=Na +K-SO₄-Cl

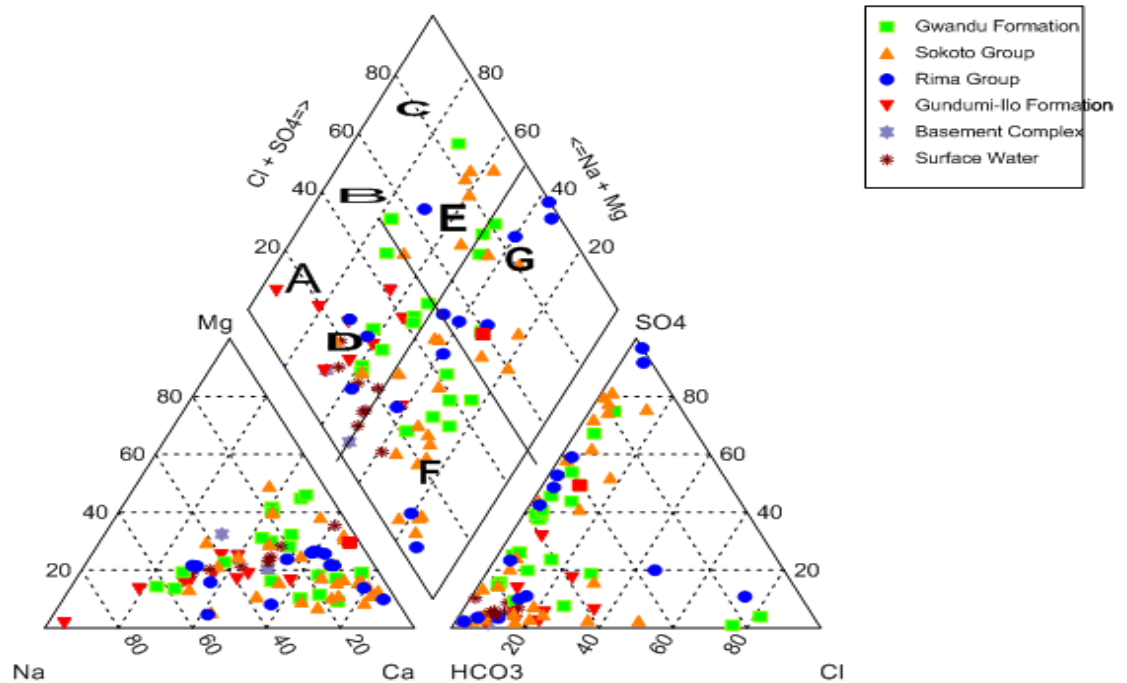


Figure 4.24 Piper diagram of the different water types in the study area.

The Piper diagram (Fig. 4.24) shows that the water types in this study that are significantly distinguished by the positions they occupy in the diamond shape were: A- Ca+Mg-HCO₃; D- Ca+Mg, Na+K-HCO₃; E- Ca+Mg, Na+K-SO₄; Na+K-SO₄-Cl and F- Na-HCO₃ (Fig. 4.24).

These facies were generally grouped into three:

- i. Group 1: AD facie includes-Ca+Mg-HCO₃; Ca+Mg, Na+K-HCO₃ water type
- ii. Group 2: EG facie includes-Ca+Mg, Na+K-SO₄; Na+K-SO₄-Cl water type and
- iii. Group 3: F facie contains Na+K-HCO₃ water type.

About 44% of the groundwater in the area plot in the water type AD of the diamond field. This water type is characteristic of freshwaters generated from carbonate rocks like limestone that is common in the area studied; 30% of EG water type observed may be from evaporite rock like Gypsum which according to previous authors characterizes the area; 26.03% of F water type observed is typical of water that has undergone the cation exchange process. The change in water composition of the waters in Sokoto Basin is due to water-rock interactions and cation exchange process as has also been suggested by previous authors in related studies (Anderson and Ogilbee, 1973; Kogbe, 1979; Darling *et al.*, 1996; Gizaw, 1996; Herczeg and Edmunds, 2000; Cloutier *et al.* (2006); Rango *et al.*, 2009, Loh *et al.*, 2012). Ca-(Mg)-(Na)-HCO₃ type waters from the basin are mostly as a result of weathering of basalts of igneous rock origin in the study area (Kogbe, 1979) and related areas (e.g.; Peccerillo *et al.*, 2003; Kersten, 2009). The transition to Na-HCO₃-type waters mainly found on the Basement Complex on the other hand is most likely due to a combination of several processes (Toran and Saunders, 1999). The increase in Na⁺ concentrations is attributable partly to the dissolution of Na-feldspars by the high CO₂ partial pressure (Darling *et al.*, 1996; Gizaw, 1996, Mazor, 2004). Cation exchange of Ca²⁺ for Na⁺ on clay minerals is another process which may be responsible for a change in relative cation contents in groundwater (Rango *et al.*, 2009). The

presence of clay minerals that are able to exchange cations, like illite, as well as secondary carbonates, has been shown in drilling cores taken from the Gundumi-Ilo Formation (Anderson and Ogilbee, 1973; Kogbe, 1979). Due to the significant lowering of Ca^{2+} and Mg^{2+} concentrations in the groundwaters, we consider that precipitation and ion exchange contribute considerably to the source of Ca-dominated to Na-dominated groundwaters in Gundumi-Ilo Formation especially.

4.4.7 General characterization of waters of the basin by Isotope approach

In this study, with the aid of conventional approach using Global meteoric line diagram, composition of stable isotope ($\delta^{18}\text{O}$, $\delta^2\text{H}$) in the basin were used to categorized the waters into three distinct types as evidenced in (Fig. 4.25).

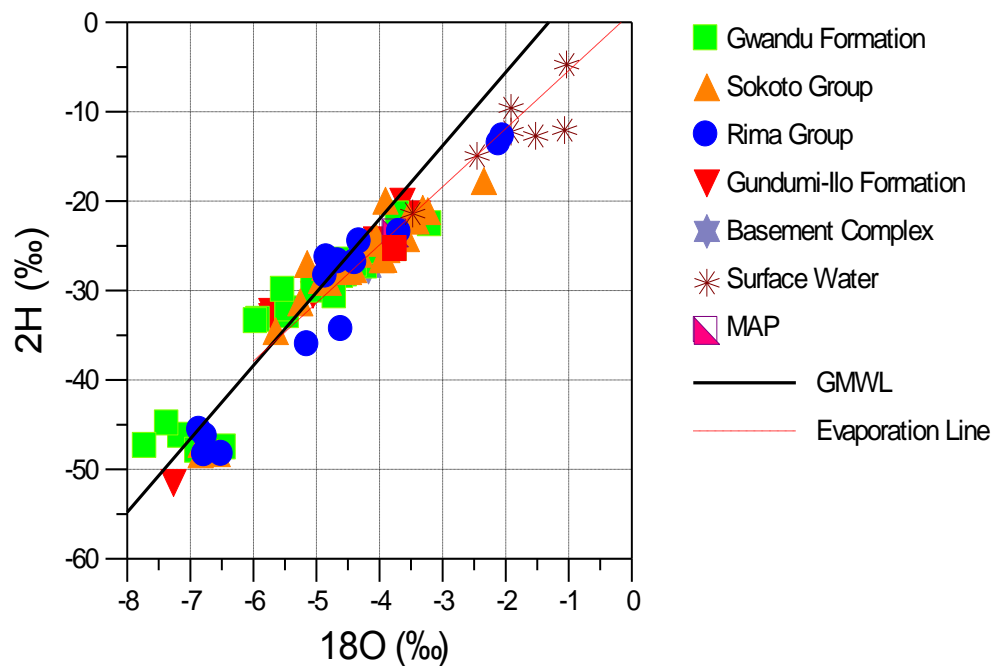


Figure 4.25: Plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ of waters in the study area

The identified groups were generally categorized as:

- i. Modern Waters: Moderately depleted in isotope signature
- ii. Paleowaters-More depleted than the former
- iii. Evaporated Waters enriched in heavy isotope and are least mineralized.

Paleowaters cover 14.94% of the entire sample; this type of water is more depleted in isotope signature compared to any other categories cluster identified in this study. The wells which tap water from the Gwandu Formation, Sokoto Group, Rima Group and Gundumi-Ilo Formation that are in this group are highly depleted in isotope signature, with $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ranging from -48.26‰ to -46.96‰ (mean= -47.13‰) and -7.72‰ to -6.84‰ (mean -6.87‰) relative to others. Moderately depleted waters cover 74.71% of total wells sampled. They include, mostly wells tapping the Gwandu Formation, Sokoto group, Rima Group and Gundumi-Ilo Formation which are less depleted in isotopic signature (compared to the former) with $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ranging from -37.12 to -20.75‰ (Mean=-27.26‰) and -6.59 to -3.20‰ (Mean=-4.49‰). Enriched waters consist of 10.34% of mostly surface waters with $\delta^2\text{H}$ from -17.65‰ to 6.75‰ (-9.79‰) and $\delta^{18}\text{O}$ from -3.52‰ to -1.05‰ (Mean= -2.89‰). They exhibit a high level of evaporation (evidence in low d-excess compare to others), which is suggestive of short residence time (Adomako *et al.*, 2011). Leibundgut *et al.*, (2009) suggested in the case of limited data, data from the IAEA GNIP/WMO (2006) network can be retrieved and used for analysis with similar atmospheric circulation patterns. Onugba *et al.* (1990); IAEA atlas of hydrology (2007); and Sokona *et al.*, (2008); and others were retrieved to bridge gap in precipitation data. The weighted mean values for precipitation (MAP) are -3.76‰ for ^{18}O and -23.50 for ^2H , (Onugba *et al.*, 1990). The similar isotopic signature peculiar to each group suggest the existence of interaction between the aquifers of the group.

The distinct Local Meteoric Water Lines (LMWL) was useful in characterizing the waters of the Sokoto Basin in the study area, (Gat, 2010). The LMWLs were observed from the overall

data from the study area using the least-square- fit linear regression (Celle-Jeonathan *et al.*, 2001) between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ to defined equations (4.4, 4.5, 4.6 and 4.7) of Gundumi-Ilo Meteoric Water Line (GuMWL), Rima Meteoric Water Line (RmMWL) Sokoto Meteoric Water Line (SkMWL) and Gwandu Meteoric Water Line (GwMWL). Where r is the coefficient of correlation, n is the number of measured points.

$$\delta^2\text{H} = 8\delta^{18}\text{O} + 10 \quad (\text{Craig, 1961}) \quad \text{equ 4.3 (Standard)}$$

$$\delta^2\text{H} = 6.87\delta^{18}\text{O} + 3.77; (r = 0.96, n = 11) \quad \text{equ 4.4}$$

$$\delta^2\text{H} = 7.46\delta^{18}\text{O} + 4.53; (r = 0.96, n = 14) \quad \text{equ 4.5}$$

$$\delta^2\text{H} = 6.92\delta^{18}\text{O} + 3.07 (r = 0.94, n = 27) \quad \text{equ 4.6}$$

$$\delta^2\text{H} = 6.3\delta^{18}\text{O} + 0.51 (r = 0.94, n = 25) \quad \text{equ 4.7}$$

$$\delta^2\text{H} = 4.05\delta^{18}\text{O} - 4.72 (r = 0.95, n = 8) \quad \text{equ 4.8}$$

The slopes for ground waters of Sokoto Basin ranged between 6.3 and 7.46 equations (4.7 and 4.5) which are low compare to global slope value standard of 8 (equation 4.3). The evaporation line is defined by 'equation 4.8'. The groundwater sample (as observed in Sokoto and Rima Groups) that plots in line with the surface waters gives evidence of an evaporative feature.

The lower slope and deuterium excess than the standard slope (8) and d-excess (10‰) (Craig, 1961), may be attributed the influence of evaporation (Mafia *et al.*, 2004; Sokona *et al.*, 2008; Hoefs, 2009; Al-Gamal, 2011 and Yidana, 2013).

The surface water (SfW) appears to be enriched in heavy isotope compare to ground water which is more depleted in heavy isotope. This is because the rivers and dams sampled are much more exposed to high effects of evaporation than groundwater (Gat, 2010).

4.5 Assessing Possibility of Renewal of the Aquifer and Interaction between Aquifers of the Basin.

In the interest of realizing second objective set down in this study, the evidences supporting possibility of renewal of the Continental Aquifer; and inter-relationships between Aquifers of the basin are presented and discussed.

4.5.1 Evidence using $\delta^{18}\text{O}$ (‰) versus depth

The relationship between depths to water level in meters versus $\delta^{18}\text{O}$ is shown as Fig4.26. A scrutiny of this figure reveals a clear cut relationship in which waters of different values of isotope signature interacted down to depth of about 150m. Similar values of isotope and chemical data suggest interconnection whereas dissimilarity indicates no interconnection, (Kumar, 2011).

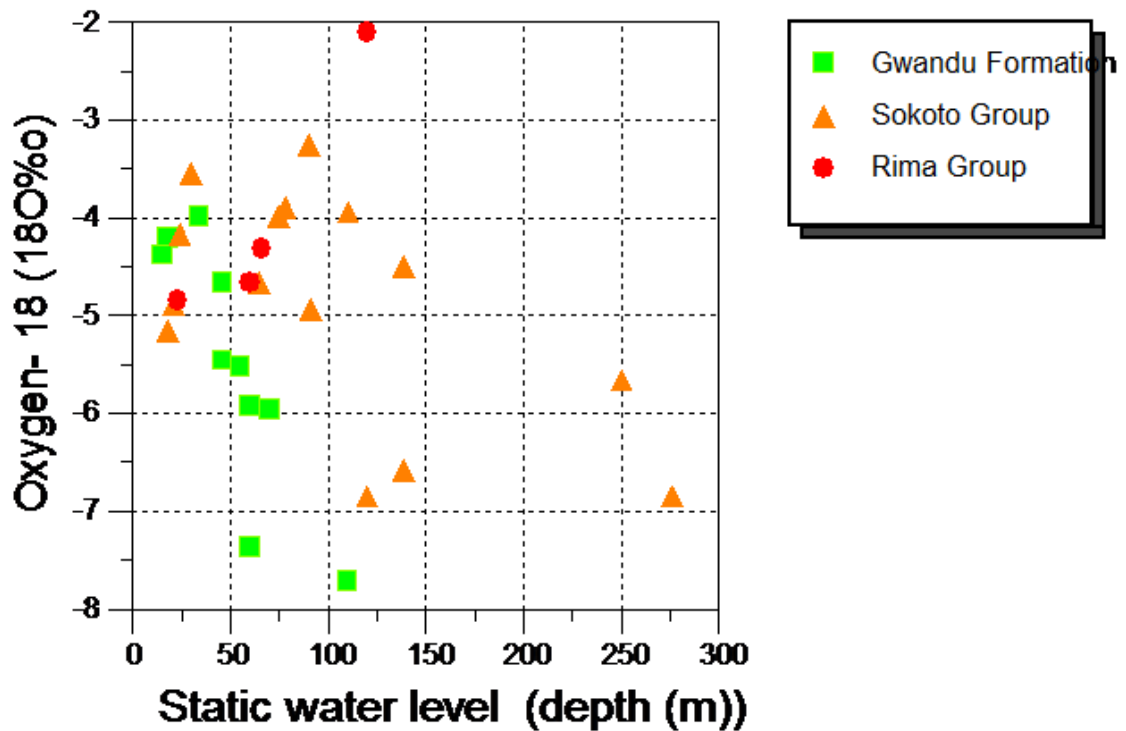


Figure 4.26 Plot of water level depth, versus $\delta^{18}\text{O}$ (‰) in the study area.

The range of stable isotopes contents varies as a result of interconnection between the waters depleted in heavy isotopes (reflective in more negative value of isotopic signature) with waters enriched with heavy isotopes, (Al-Gamal, 2011). It also reflects a considerable fraction of modern water that continues to interact with the already existing paleowater down to a depth of 150m. Thus, the interaction process has extended down to include aquifer's saturated depth, (Neal *et al.*, 2005).

The aquifer also exhibits an altitude effect according to which more depleted stable isotope signatures are associated with high altitudes. Thus, Oxygen-18 composition of rain water that recharges each group is affected by altitude. This could also account for the observed difference in stable isotopes. In view of the above, it then confirms that the aquifer receives a considerable fraction of modern water recharge, which is also in line with deductions of previous authors: (Payne and Yurtsever 1974; Bortolami *et al.*, 1978; Leontiadis *et al.* 1983; Oteze, 1989b; Onugba *et al.*, 1990; Nti, 2005, Al -Gamal, 2011; Wassenaar *et al.*, 2011).

4.5.2 Evidence using salinity versus $\delta^{18}\text{O}$

Salinity increases as evaporation intensifies and we can generalize the relationship to state that water with an increased $\delta^{18}\text{O}$ is saltier than water with a lower $\delta^{18}\text{O}$. A scrutiny of Fig (4.27) shows the isotope data in ground and surface water vary with salinity concentration.

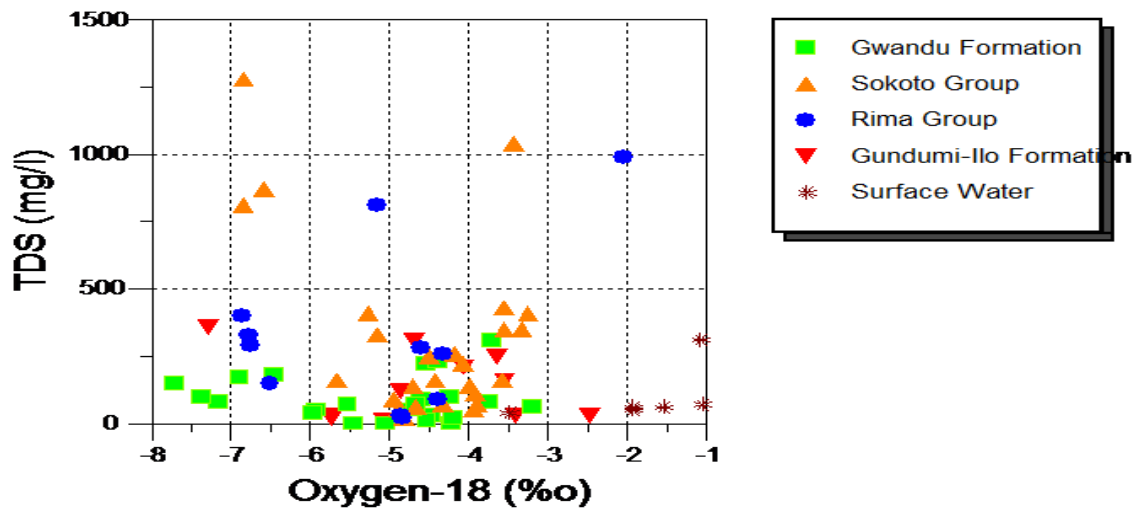


Figure 4.27 Salinity in mg/L versus $\delta^{18}\text{O}$ for the waters in the study area

Although difference in salinity exists, water clusters have closely related isotopic signatures. However, this does not occur in the whole system as can be seen in some parts of the aquifer (Fig. 4.27) where aquifer shows the same isotopic signature versus a wide range of salinity variations. Al-Gamal (2011) suggests that such an occurrence can be described as homogenous and heterogeneous interaction of water chemistry within and between the aquifers.

However, aquifer salinization cannot be explained by evaporation mechanism alone. Dissolution of salty sediments is likely to contribute to the excess salinity. Besides, recent recharging water of low or high salinity could lead to wide range in salinities.

A detailed examination of the Fig 4.27 can lead to definition of the original isotopic composition at zero salinity which represents the starting isotopic composition of rainwater at the time of recharge. The $\delta^{18}\text{O}$ values at zero salinity ranges between -3.5‰ and -6‰. It can be concluded from isotope composition and salinity content that the ground water in the aquifer system has three clusters.

- i. The paleowaters define by there high depleted Oxygen -18 with low and high saline content.
- ii. Moderately depleted fresh waters and brackish waters in isotope signature due to evaporites included in the litho-stratigraphic sequence of paleocene sediments and
- iii. The low mineralized enriched waters.

This concurs with the findings of Alagbe, (2004) that the groundwaters of part of Sokoto Basin consist of mixtures of waters of different sources and having different salinities. Other previous studies indicate that Taloka (North East to Wurno irrigation project) and Hamma – Ali (South-West of Wurno irrigation project) are predominantly Paleowater (Hanidu (2005) and Maduabuchi (2006)) Adelana *et al*(2003), reported that Rima Group (Taloka) especially around Wurno and Goronyo irrigation schemes is presupposed to be paleowaters, almost ruling out rain recharge. Oteze, (1975), and JICA, (1990) reported that surface waters are fed principally by the groundwater. Sokona *et al.*, (2008) observed that the Rima River is recharging part of the alluvial aquifer in the Sokoto Basin, while the portion of paleowater related to the Continental Intercalaire receives no recharge. This converse fact is possible, because the later observation was based on the relationship between salinity and $\delta^{18}\text{O}$ the former was based on relationship between $\delta^{18}\text{O}$ and $\delta^2\text{H}$.

4.5.3 Evidence using characteristic d-excess

The d-excess value can be calculated from equation 4.7 (Dansgaard, 1964). The d-excess value can be greater than 10‰ (that is, it can range from 14‰ -15‰) in tropical African region, (Onugba *et al*, 1990). D-excess value of water vapor is a function of humidity, surface temperature, isotopic compositions of ambient water vapor and evaporating water (Al- Gamal, 2011). The d-excess is capable of indicating the origin of water vapor responsible for precipitation in a given locality. The negative value of d-excess reflects that sample source is

from local isolated moist air masses. Accordingly, Dansgaard(1964) define d-value using equation 4.9.

$$d = \delta^2\text{H} - 8\delta^{18}\text{O} \quad \text{Eqn. 4.9}$$

In Appendix XI, the calculated d-excess value for the study area were presented.

Generally, the calculated d-excess values fall within 14 and 15. It ranged between -20.1‰ and +14.39‰. The majority of the d-excess values from the study area are positive while a few values are negative (Fig 4.28). The negative values was attributed to the recent rainfall, (Gammons, 2006).

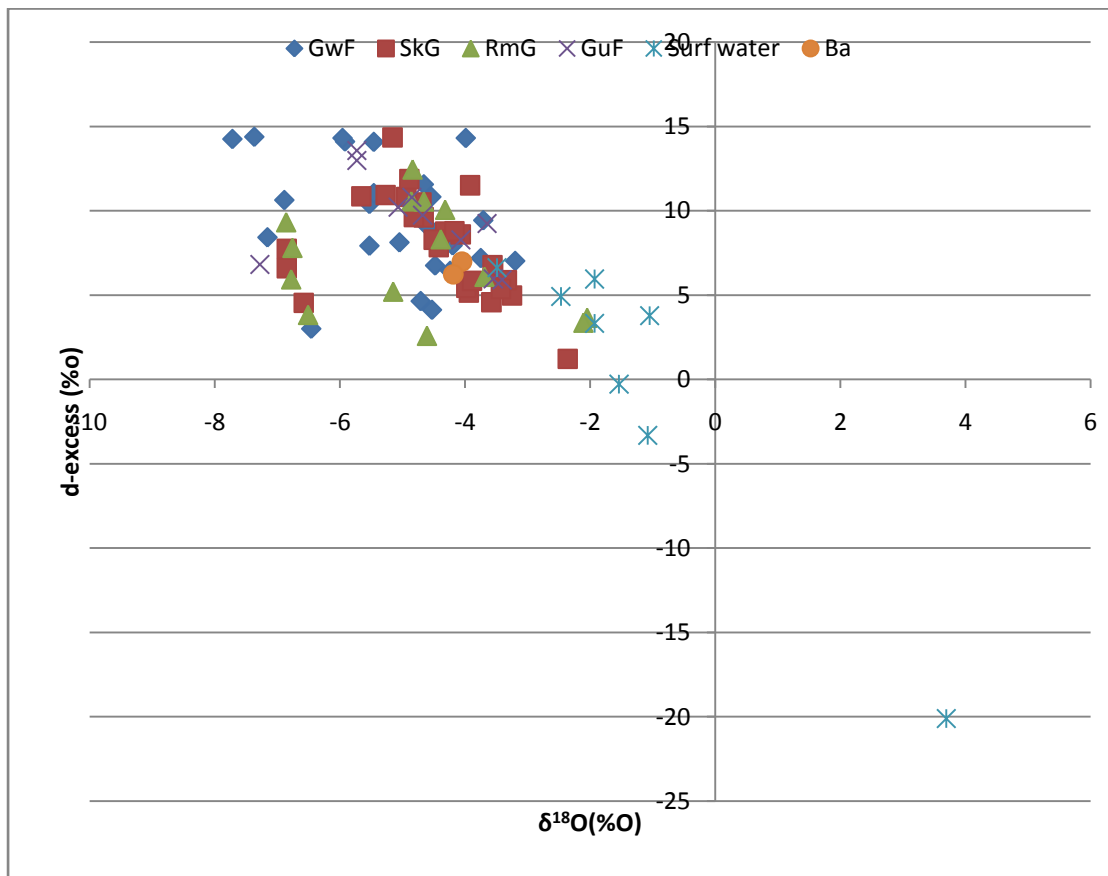


Figure 4.28 Relationship between $\delta^{18}\text{O}$ and d-excess for the waters in the study area.

The low ‘d-excess’ values ($\leq 6\text{‰}$) observed in the waters of the study area suggest that there is significant evaporation of rainwater leaving the residual groundwater with lower values of

'd-excess' (Al-Gamal, 2011). High 'd-excess' values indicate that the evaporative flux from continental waters is the major contributor to the total moisture balance of air mass, (Onugba *et al.*, 1990).

The d-excess >10‰ is an indication of recharge source from mixed oceanic and continental vapor. In this case, high d-excess values (>10‰) indicate that the evaporative flux from east of the study area contribute to recharge source. Sokona *et al.*, (2008) suggested that ground waters recharge in Sokoto basin is of the same origin of vapor; and that the shallow aquifers in the Iullemeden Basin receive a considerable recharge from the surface water bodies represented by the Rima and Sokoto rivers which discharge into the River Niger. The maximum, minimum and mean d-excess values for surface water are 6.62‰, -0.28‰ and 4.05‰ respectively. The calculated d-excess values for precipitation (ranged from -26.48‰ to 20.98‰ (Onugba *et al.*, 1990)). The observed trend in results reflects interaction of recent recharge waters, of $\delta^{18}\text{O}$ derived from rainfall of low mineralization (Adelana *et al.*, 2003) with Paleo-waters, (Sokona, *et al.*, 2008; Hoefs, 2009; and Wassenaar, *et al.*, 2011). In lieu with the above, (Sokona *et al.*, 2008), also noted that the groundwaters of the Iullemeden Basin has major components; the modern water of Quaternary age and the paleowaters of the Continental Intercalaire and Complex Terminal of Paleocene.

4.5.3 Evidence using Conventional Relationship between $\delta^{18}\text{O}$ and δD .

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions of meteoric waters has long been known to vary in a systematic manner, in which meteoric waters fall close to the global meteoric water line (GMWL, $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$) (Craig, 1961a; Rozanski *et al.*, 1993 e.t.c). Most of the groundwater samples tapping different aquifers plot on or above the GMWL while a considerable number plot slightly below the GMWL (Fig.4.29). The deviation of some of the

samples from the GMWL suggests that evaporation occurs prior to or during infiltration; or that recharge represents an interaction of isotopically enriched and depleted waters. A further scrutiny of Fig.4.29 reveals that, the majority of groundwater samples taken from Gwandu Formation, Sokoto Group, Rima Group and Gundumi-Ilo Formation, plot slightly below the GMWL which can be associated with marine air mass coming from the Mediterranean Sea that eventually leads to a low slope and low intercept in the local meteoric water line (LGWLs).

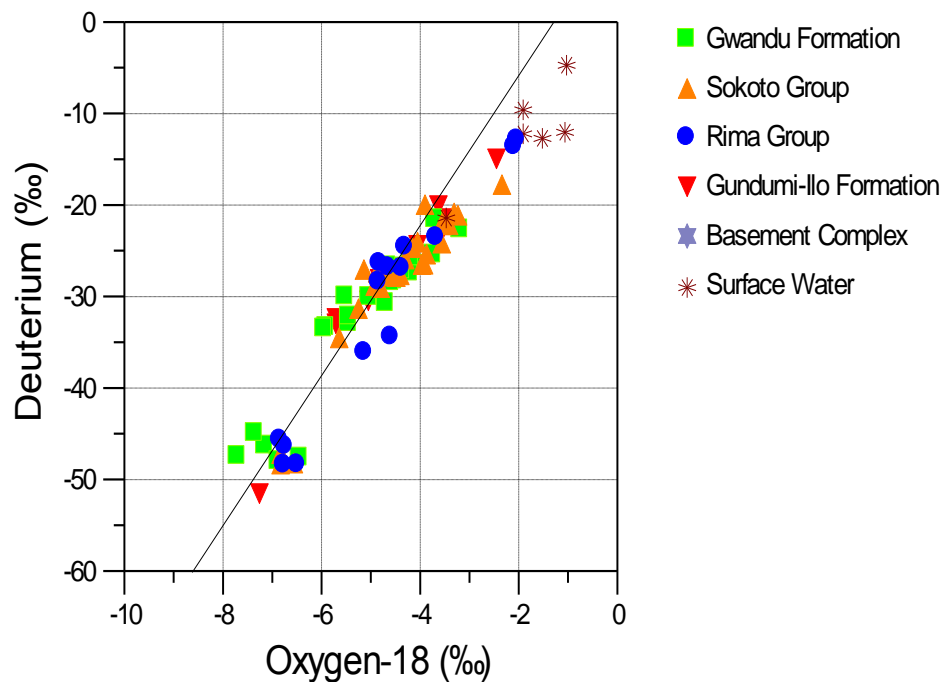


Figure 4.29 Meteoric water line plot of sampled waters in the study area

The foregoing is also supported by the data of d-excess, having higher values >10‰ in some parts of the aquifer as relative to the continental air mass; and lower d-excess values (<6‰) at the other locations of the various aquifer type as subjected to marine air mass. As such,

the observed behavior indicates an interconnection of recent recharge waters, of $\delta^{18}\text{O}$ derived from present day rainfall of low mineralization, with paleowaters, (Al-Gamal, 2011).

4.5.5 Evaluation Using Unstable Isotope Signature of Tritium

The natural production of tritium introduces about 5 TU to precipitation and surface water. The nuclear bomb tests, which began in 1952 in the northern hemisphere, added large amounts of tritium to the atmosphere. Semiquantitative dating according to Mazor (2003) was used to classify Tritium content in this study:

- i. Water with zero tritium (in practice <0.5 TU) has a pre-1952 age.
- ii. Water with significant tritium concentrations (in practice >10 TU) is of a post-1952 age.
- iii. Water with little, but measurable, tritium (0.5–10 TU) seems to be a mixture of pre-1952 and post-1952 water.

Presented in Fig. 4.30 is histogram classification of tritium concentration measured in the study area.

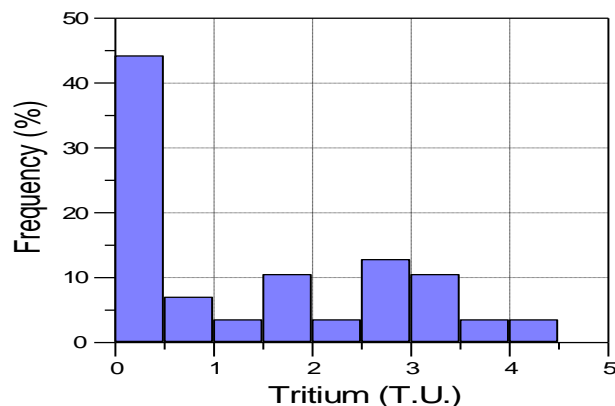


Figure 4.30 Histogram of Tritium Concentration Measured

The Figure obviously shows that 44% of the waters are waters of pre 1952 era origin interacting with interconnected waters of pre1952 and post 1952 era origin in accordance with Mazor (2004) semi-quantitative dating interpretation.

The present concentration of tritium in Nigeria is not well known. However, Tritium concentration in the study area generally is within the range of -3.24 to 4.1TU (mean=1.24TU) (see Table 4.15). The descriptive statistics summary of isotope composition is presented in Table 4.15.

Table 4.15 Descriptive statistics summary of isotope composition in Sokoto Basin

Formation code	Parameter	Unit	Max	Min	Mean	STD
Ba	³ H	T.U.	2.76	1.95	2.355	0.573
	¹⁸ O	‰	-4.05	-4.19	-4.12	0.099
	² H	‰	-25.4	-27.3	-26.36	1.322
GuF	³ H	T.U.	3.59	-0.37	0.63	1.23
	¹⁸ O	‰	-3.41	-7.28	-4.8	1.217
	² H	‰	-19.96	-51.4	-29.1	9.06
RmG	³ H	T.U.	3.6	-0.27	1.082	1.43
	¹⁸ O	‰	-2.05	-6.86	-4.83	1.557
	² H	‰	-12.75	-48.3	-31.5	12.02
SkG	³ H	T.U.	4.1	-3.89	1.236	1.725
	¹⁸ O	‰	-2.36	-6.85	-4.47	1.094
	² H	‰	-17.65	-48.2	-27.86	8.03
GwF	³ H	T.U.	3.43	-0.42	0.849	1.186
	¹⁸ O	‰	-3.2	-26.46	-6.03	4.42
	² H	‰	-3.99	-47.9	-30.94	9.86
Surface Water	³ H	T.U.	4.1	2.54	3.244	0.571
	¹⁸ O	‰	3.69	-3.49	-1.225	2.138
	² H	‰	9.42	-21.3	-9.69	9.04

Abbreviation explained: Ba= basement complex, GuF= Gundumi-Ilo Formation, RmG= Rima Group, SkG= Sokoto Group, GwF= Gwandu Formation, STD= standard deviation, Mean= arithmetic mean, max= maximum, min= minimum.

A plot of $\delta^{18}\text{O}\text{‰}$ versus ^3H expressed as tritium unit (TU) (Fig 4.31) shows an interaction between paleowaters of $\delta^{18}\text{O}$ from -8‰ to -4‰ and tritium value from 0TU-0.5TU with young waters of $\delta^{18}\text{O}$ from -8‰ to -2‰ and tritium value from 0.5TU to 4.5TU. This contrasts the observation of Sokona *et al.*, (2008) and others.

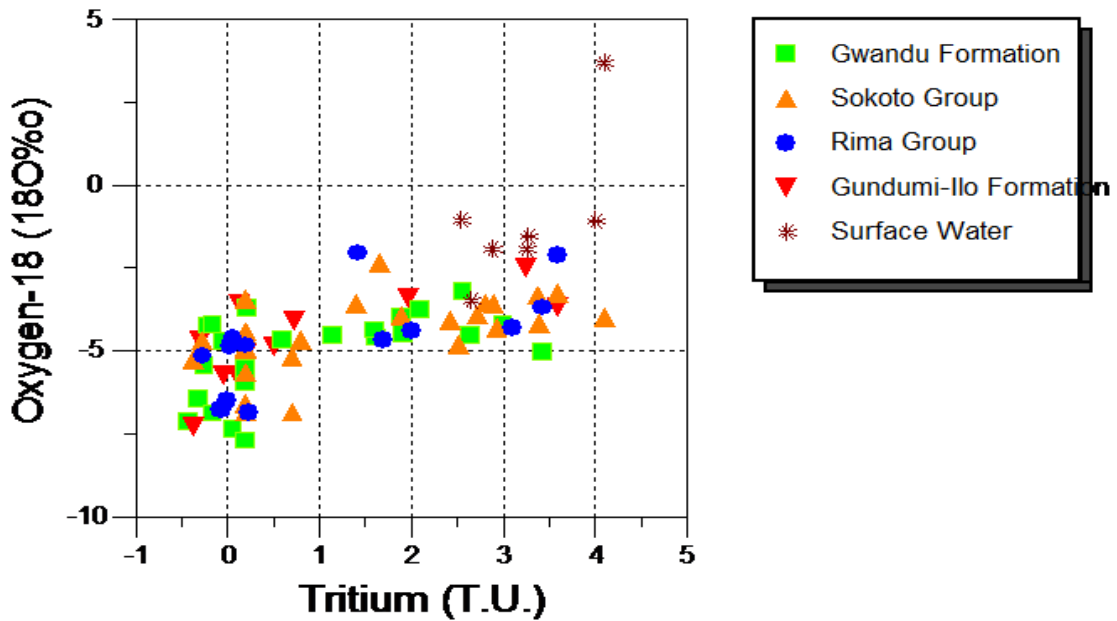


Fig 4.31 Relationship between $\delta^{18}\text{O}\text{‰}$ and ^3H (TU) of waters in the study area.

Consequently, the observed behavior indicates that there is interaction between recent recharge waters derived from present day rainfall of low mineralization, with paleowaters.

4.5.6 Statistical evidence of aquifer renewal and relationship among the aquifers

Rima Group distribution is positively skewed than the corresponding aquifers (GwF, SkG and RmG) distribution, as is evidenced by the fact that the distribution as shown in the box plots in Figs 4.32 and 4.33 has RmG stable isotope distribution long tail more to the positive values of the central maximum than to the negative values; but that Gwandu Formation is more negatively skewed compared to other Formation types. The cause of the skewed distributions is extreme values, (Al Gamal, 2011). The extreme values were attributed to seasonal variation according to Onugba *et al*, (1990).

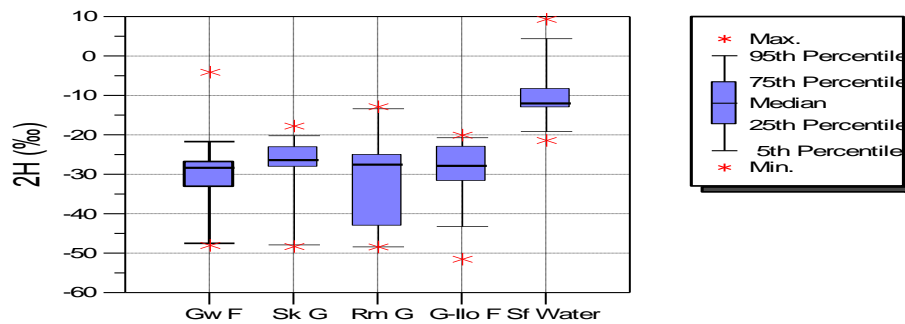


Figure 4.32 Boxplots of $\delta^2\text{H}$ isotope representation of interaction among the aquifers in the study area.

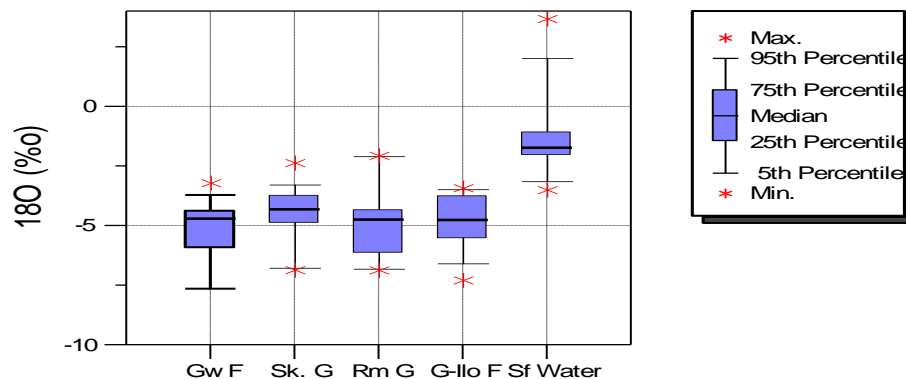


Figure 4.33 Boxplots of $\delta^{18}\text{O}$ isotope representation of interaction among the aquifers in the study area.

The similar range observed in δ -values of ^{18}O and ^2H between the aquifers (Gw.F, Sk.G, Rm G and Gu.F (Fig, 4.32) suggest that the waters are interacting. This range of stable isotope contents can be attributed to the interactions between palaeowaters highly depleted in delta values with more recent water comparatively enriched in delta values. Furthermore, it may reflect the possibility of interaction between water precipitated at different altitudes, which in turn may also account for the observed differences in stable isotopes.

Maduabuchi(2006) suggested that variations observed in isotope signature may be due to heterogeneity of recharge conditions of isotopically different rainfall(-9.97‰ to 11.11‰ for

$\delta^{18}\text{O}$ and -58.3‰ to 62.4‰ for $\delta^2\text{H}$) (Onugba *et al*, 1990), and events which enter the system after being subject to evaporation. Darling, (2011) linked the variation in isotopic signature to an interaction between palaeo-water highly depleted in delta values with more recent water comparatively enriched in delta values; and Drever (1988), reported that because of shifts in climatic patterns, precipitation during the Pleistocene and Tertiary differed cyclically in isotopic composition from present day precipitation. Younes (2012) and Nyende (2013) associated the variations in the isotope signature in the water to an interaction between water precipitated and mixed isotopic signatures from several precipitation events. The surface water data are the most enriched in the heavier isotopes as is obvious in Figures 4.32 and 4.33. This may be attributed to the full exposure of the surface water to high atmospheric temperatures and low humidities throughout the year. Yidana (2013) observed a similar trend in the range of surface and ground water.

4.6 Assessment and evaluation of water chemical quality

This sub-section is structured to achieve the third objective of this study: to assess and evaluate the contaminant concentrations in the water systems and ascertain the usefulness of the waters for various uses. The change in water quality is usually as a result of alteration in natural physical and chemical states of the water; as well as any alteration that may have occurred due to human activities (anthropogenic input). The physicochemical composition in waters was assessed to determine its adequacy for drinking, domestic, industrial, and agricultural purposes. Each type of use requires certain water quality criteria, which determine whether the water is suitable for the purpose (UNESCO/WHO, 1978). In this study, other physico-chemical concentrations measured in surface and groundwater samples in Sokoto Basin are fully presented in (Appendix. XIV). The waters were assessed and evaluated for different uses by the application of water quality standards established by various local (SON,

2007) and international scientific organizations (eg; WHO, 2004) accepted standard criteria for water quality assessment.

4.6.1 Assessment and evaluation of contaminants concentrations in the study area

i. Chloride (Cl): In this study, Chloride ion (Cl⁻) concentration was between 0.37mg/L and 76.50mg/L (mean=8.42mg/L), (see Appendix XIV). The least concentration of Chloride was measured in Gwandu Formation (at Tangaza an artisan well); while the maximum concentration was measured in Sokoto Group at Gigane, see Table 4.16 extracted from Appendix, XIV

Table 4.16 Representative Physico-Chemical constituents of waters in the study area

Station ID	Location	Sample ID	Cl mg/L
GWSS4	Tangaza	GW	0.37
GWSS67	Gigane	SK	76.5
GWSS13	Isa	GU	26.81
GWSS14	Tarshar B	GU	12.65
GWSS3	Gidan Madi	GW	36.24
GWSS35	Shagari	GW	4.9
GWSS43	Dageri	GW	3.66
GWSS84	SokotoTown1	SK	17.93
GWSS85	SokotoTown2	SK	27.37
GWSS7	Mammasuka	SK	22.3
GWSS17	Tsamaye	SK	3.21
GWSS67	Gigane	SK	76.5
GWSS19	Taloka	RM	21.72
GWSS55	Kebbe	RM	31.24
Minimum			0.37
Maximum			76.5
Arithmetic Mean			8.42

GU= Gundumi-Ilo, GW= Gwandu, Sk= Sokoto Group, Rm= Rima Group, GWSS=Groundwater sample station.

The arithmetic mean of Cl⁻ concentration is within acceptable limit for WHO (250mg/L), BIS(250mg/L), EU(250mg/L) and SON (250mg/L) water quality standard for drinking. This implies that the waters are of satisfactory quality in terms of their chloride contents. This is in

accordance with findings of previous researchers in an aspect of the basin (Rajiet *et al.*, 2015; Adejo *et al.*, 2015; Ipinjolu and Argungu, 1998; Abubakar and Ipinjolu, 2015 and others).

The limits of chloride have been put more from the point of view of taste rather than its adverse effect on human health, (Singhal and Gupta, 2010). Water with chloride concentration more than 250 mg/L (Table, 4.17) will be saline in taste, (Chinn, 2003) but acceptable for stock (Mazor, 2004).

Table 4.17: Water Quality Standards of various constituents (mg/L) for drinking-water

Parameter (mg/L)	European Union (2003)	USEPA (2002)	WHO (2004)	BIS (1991)	SON (2007)
TDS	-	500	1000	500	500
pH	-	6.5-8.5	6.5-8.5	6.5-8.5	6.5-9.2
Total Hardness(CaCO ₃)	-	-	500	300	150
Ca	-	--	75-200	75	20
Mg	-	-	-	30	150
Na	200	-	200	-	-
Cl	250	250	250	250	250
SO ₄	250	250	400	150	-
NO ₃	50	44	50	45	50
Fe	0.2	0.2	0.3	0.3	0.3
F	1.5	4	1.5	1.2	1.5
Pb	0.01	0.01	0.01	0.1	<0.5
Hg	0.001	0.002	0.001	0.001	<0.5
Zn	-	5	5	5	15
Cu	-	-	1	0.05	1.5
Cd	0.005	0.005	0.003	0.01	0.01
As	0.05	0.01	0.01	0.05	0.05
Cr	0.01	-	0.05	0.05	0.05
CN	-	0.2	0.05	0.05	0.5

USEPA-Environmental Protection Agency, USA, WHO - World Health Organization,,BIS-Bureau of Indian Standards, SON-Standard Organization of Nigeria.

Generally, high chloride concentration in waters are usually attributed to industrial, domestic wastes, leaching from upper soil layers in dry climates and transported by recharge water.

Halite is mainly the source of chloride that water contains by interaction with rocks (Mazor, 2004).

ii. Nitrate (NO₃): Nitrate (NO₃) is one of the most common groundwater contaminants in the world and its presence in higher concentrations (>50mg/L) poses human health and ecological risks. Studies in different parts of the USA, Europe, Asia and Africa show that agricultural fertilizers and urban septic tanks are the primary sources of large nitrate concentrations in surface and groundwaters. Gustafson (1993) observed that nitrate ions are common contaminants in drinking water closely associated with agricultural activities. Nitrate concentrations above the recommended value of 45mg/L is dangerous to pregnant women and poses a serious health threat to infants less than 6 months of age because of its ability to cause methanoglobinaemia or blue baby syndrome, in which blood loses its ability to carry sufficient oxygen (Fecham, *et al.*, 1986). However, nitrate in irrigation water is usually considered an asset because of its value as a fertilizer (Bertoldi *et al.* 1991).

The range of results obtained for NO₃ in this study vary between 0.00mg/L to 259.03mg/L (mean= 22.14mg/L). The least concentration was measured in the Gwandu Formation (at Tangaza, an artisan well) while the highest concentration was measured in Sokoto Group at Gigane well. The maximum value exceeded the permissible (WHO, 2004) and (SON, 2007) limit for water quality standard of 50mg/L. Gigane is surrounded by farm lands, it is about 1.5km from an abattoir and about 2.2km from Rima river. Thus, the enriched NO₃ content obtained from Gigane well water and a few other locations were traced to point and non-point sources in the study area such as the nearby farm; abattoir waste water; wastes from animal rearing; indiscriminate siting of wells especially close to septic tanks and the drainage system (gutter); and others (see Figs 4.34 and 4.35).

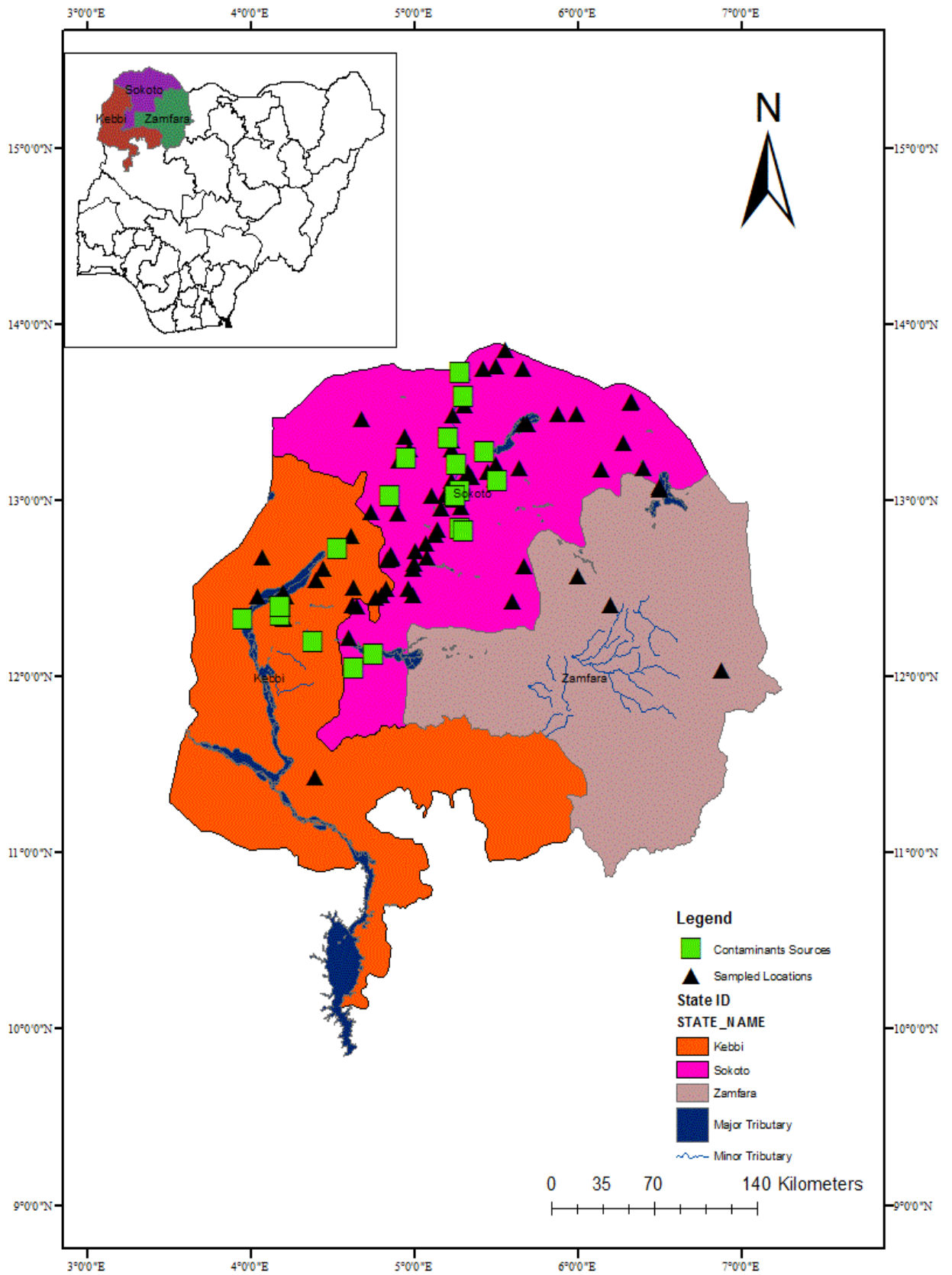


Figure 4.34 Sampled locations with possible contaminant sources

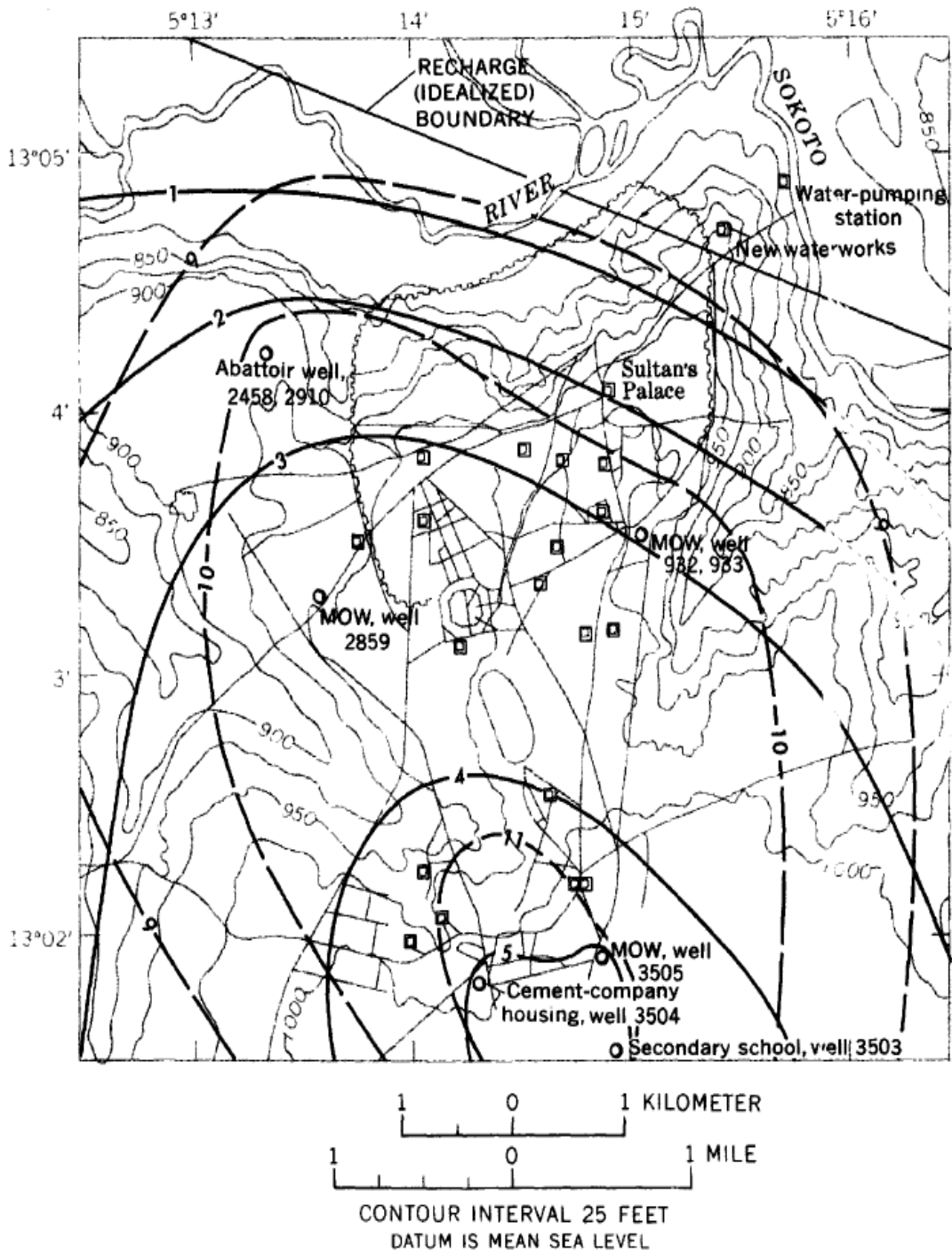


Figure 4.35 Identified Contaminant sources map, (Anderson and Ogilbee, 1973)

Nitrate (NO₃) concentration observed in some locations as shown in Table 4.18 exceed the international (WHO, 2004) and local permissible limits (SON, 2007) of 50mg/L for drinking water. For instance, in Rima Group (at Kebbe) NO₃ Concentration was 192.67mg/L; in the Sokoto Group (Sokoto Town I, Sokoto Town II, Mammasuka and Kalambaina); nitrate concentrations were 65.27mg/L, 91.97mg/L; 69.43mg/L and 80.04mg/L respectively; and in the Gwandu Formation, nitrate concentration were measured at respective locations including Shagari (51.48mg/L), Gidan Madi (87.32mg/L), and Ganbuwa(71.64mg/L) (see Appendix XIV).

Table 4.18 Stations with high Nitrate concentration

Stn ID	Location	Sample ID	NO ₃ mg/l
GWSS3	Gidan Mai	GW	87.32
GWSS35	Shagari	GW	51.48
GWSS84	Sokoto Town	SK	65.27
GWSS85	Sokoto Town	SK	91.97
GWSS7	Mammasuka	SK	69.45
GWSS30	Kalambaina	SK	80.04
GWSS67	Gigane	SK	259.03
GWSS55	Kebbe	RM	192.67

These stations GWSS3, GWSS35, GWSS84, GWSS85, GWSS7, GWSS30, GWSS67 and GWSS55 were not within acceptable limits of 50mg/L set by WHO (2004), and SON (2007) respectively, (Table 4.18). The high concentration of nitrate obtained in these areas may be attributed to leaching from the application of organic and inorganic fertilizers in surrounding farmlands (e.g. Ministry of Agricultural farm plots which is about 0.8km from Gurum river a tributary of Sokoto and Rima river), orchards (Ministry of Agriculture orchard which is about 0.6km from Gurum river, a tributary of Sokoto and Rima rivers, orchards (Ministry of

Agriculture orchard which is about 0.6km from Gurum river), plantations, forest reserves, and poor sanitary conditions.

It is clear from Fig, 4.36 that 89.65% of waters within the area of study fall in the acceptable range for WHO (2004) and SON (2007) recommended standard for drinking water. About 8.04% were not within acceptable limit.

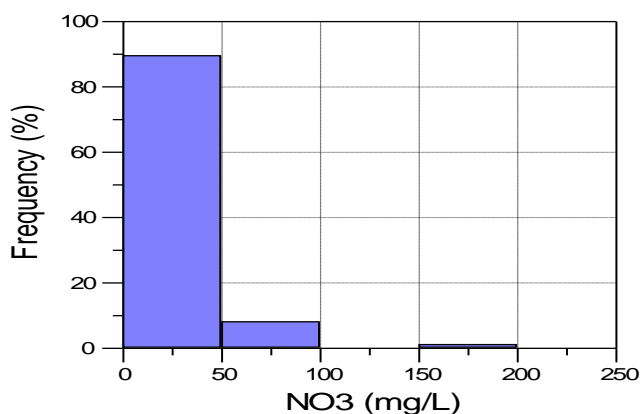


Fig 4.36 Nitrate concentration histogram plot in the study area.

Nitrogenous fertilizers have been one of the important sources of groundwater nitrate in the last two decades, (Ramesh *et al.*, 2012). In the view of the above, the high nitrates concentration measured may suggest modern water. This is confirmed by their high tritium compositions obtained and corresponding to the fore mentioned specified locations with high nitrate concentrations such as GWSS3(2.64TU); GWSS84(3.6TU), GWSS85(2.8TU), GWSS7(2.43TU), GWSS30(2.89TU), GWSS67(4.9TU) and GWSS55(3.1TU). This result is similar to that of a previous study in the area, by Raji *et al.*, (2015). The nitrate levels in Sokoto river were above the permissible limit, and the cause of high level of nitrate may be as a result of extensive farming taking place at the banks of the river since the farmers use fertilizers.

However, The highest concentration and the mean values were within the standard recommended for aquatic life (>5mg/L) (Vezeau, 1989).

iii. Fluoride: is beneficial when present in small concentrations (0.8–1.0 mg/L) in drinking water, (Singhal *et al* 2010), but it causes dental and skeletal fluorosis if present in higher amounts. Bedrock containing fluoride minerals is generally responsible for high concentrations of this ion in groundwater (Handa, 1975). Higher concentrations of fluoride in drinking water are also linked with cancer (Smedley, 1992). The permissible limit of Fluoride depends on temperature; higher intakes (sic) of fluoride can be permissible in colder climates (Hamill and Bell 1986).

In this study, the mean concentration of fluoride (0.56mg/L) is within the acceptable limits (BIS, 1991 (1.2mg/L); European Union, 2003 (1.5mg/L); SON, 2007 (1.5); USEPA, 2002(4.0mg/L) and WHO,2004 (1.5mg/L))for drinking water. The Fluoride concentration ranged between 0.07mg/L and 6.45mg/L. The measured high value concentration was observed at Gigane (GWSS67) of Sokoto Group.

The fluoride concentration in waters of the basin were further assessed for its impacts on health following Dissanayake’s (1991) classification (see Table 4.19).

Table 4.19 Fluoride composition of waters from the study area evaluated with the health implications (after Dissanayake, 1991) guideline.

Case study F (%)	F(mg/L) Concentration	Impact on health
78.16	<0.5	Dental caries
16.09	0.5–1.5	Promotes dental health
4.59	1.5–4.0	Dental fluorosis (mottling of teeth)
1.14	4.0–10.0	Dental and skeletal fluorosis (pain in back bones)
	>10.0	Crippling fluorosis

Findings from this study, showed that 78.16% and 16.09% of sampled waters may not lead to dental fluorosis while 4.59% and 1.14% of waters may lead to a surge in water-related diseases such as skeletal and dental fluorosis. The 5.73% high fluoride concentration measured conforms to the GEF (2003) report of high fluorine contents observed in water supply boreholes in the area. Most ground waters sampled have low fluoride concentrations (<0.5mg/L). Similarly, the surface waters sampled contained low concentrations of fluoride (<0.5mg/L). Fluoride in water derives mainly from dissolution of natural minerals (mostly: fluorite, apatite, and micas) in rocks and soils with which water interacts.

The high fluoride concentration measured in few locations may be due to leaching from fluoride rich rocks like Mica which is one of the minerals peculiar to basin formation types (Anderson and Ogilbee (1973); and Kogbe, (1979)). In areas of higher fluoride concentration, defluoridation can be adopted to reduce the high fluoride concentration to the barest minimum to supply safe drinking water. The most common method, adopted in India, is the Nalgonda process developed by the National Environmental Engineering Research Institute (NEERI). The Nalgonda technique comprises addition of lime and aluminum sulphate or aluminum chloride which helps in the removal of fluoride by flocculation, (Singhal and Gupta, 2010). Clinical reports indicate that adequate calcium intake reduces a risk of dental fluorosis (WHO, 2006 and Vandi, 2010). It may partly be for this reason that pregnant women are administered with calcium supplement as part of their daily routine drugs in Africa like Nigeria.

iv. Boron: Boron is an essential element for plant growth and is needed in relatively small amounts. However, it may turn toxic if present in appreciably greater amounts than needed. It is comparatively scarce in nature. Groundwater, unlike surface water, may contain toxic amount of boron (Aly, 2001). Water samples were analyzed for its boron concentrations. The

result showed that most studied waters in the study areas were within the acceptable levels(0.5mg/L).Only three samples (Gidan Ciwake (1.24mg/L); Wauru(1.03mg/L) and Rafin Duma(1.18mg/L)) in the Basin (see Appendix XIV) have Boron concentrations more than 0.5mg/L (WHO, 2004) consequently these three samples have slight to moderate degrees of restriction on use for irrigation agriculture(Ayers and Westcote, 1985).

v. Iron: Iron is one of the most abundant metals in the Earth's crust. It is found in natural fresh waters at levels ranging from 0.5 to 50mg/L. High concentration causes slight toxicity, inky flavor, bitter and astringent taste and can be remediated by aeration followed by sedimentation. The shortage of iron causes a disease called anemia and prolonged consumption of drinking water with high concentration of iron may lead to liver disease called as haemosiderosis (Ramesh *et al.*, 2012).The measured iron concentration in surface and ground waters in this study range between 0.3mg/L and 3.08mg/L.The mean Fe concentration of 0.068mg/L measured is within the WHO (2004) and SON (2007) acceptable concentration of (0.3mg/L) in drinking water. However, only a station Rafin Duma with 3.08mg/L of iron concentration exceeded the permissible limit for drinking (Appendix XIV). In ground water, the minimum measured concentration of 0.00005mg/L was in the Gwandu Formation at Tambuwal. The maximum value (3.09mg/L) measured was at Rafin-Duma. Iron may be present in drinking water as a result of the use of iron-containing coagulants or through the corrosion of steel and cast iron pipes during water distribution.

vi. Cadmium(Cd): The mean concentration (0.01mg/L) of Cd as measured is within the acceptable limits for potable water by WHO(2004) (0.003mg/L) and SON(2007) (0.003mg/L). About 24% of sampled waters have Cadmium concentration above the permissible standard of 0.003mg/L set by WHO (2004) and SON (2007) standard bodies for domestic purpose (see Table 4.20).

Table 4.20: Assessment of Cd (mg/L) in waters of Sokoto Basin by Various permissible limits

Station ID	Location	Distance(km)	Cd(mg/L)
SRI66	Balkori R		0.02
SRIS27	Rima River		0.02
SRIS28	Sokoto R.		0.02
GWSS87	YarGeda	0.3	0.01
GWSS86	Bimasa	0.4	0.02
GWSS14	Tarshar B	0.1	0.02
GWSS64	Silame	1.2	0.02
GWSS78	Ganbuwa	2.2	0.02
GWSS17	Tsamaye	0.2	0.22
GWSS51	Sifawa	1.6	0.02
GWSS52	Jabo	1	0.01
GWSS53	Dogongaji	0.2	0.01
GWSS54	Barkeji	2.2	0.01
GWSS65	Tulluwa	0.4	0.02
GWSS67	Gigane	2.2	0.02
GWSS68	Illela	0.7	0.02
GWSS69	Gidan Ciwake	0.4	0.02
GWSS70	Wauru	0.1	0.03
GWSS71	Rafin Duma	2.2	0.02
GWSS73	Rugar Kijo	0.3	0.02
GWSS75	Salah	0.2	0.02
GWSS8	Tumbulla	0.56	0.02
GWSS20	Goronyo Town	0.15	0.23
GWSS74	Bancho	2.4	0.01
GWSS79	Yabo	0.3	0.02
GWSS72	Gada	6	0.02
GWSS22	Wurno	1.6	0.02
GWSS23	Wurno (Kofar)	1.4	0.02
GWSS24	Wurno(Ka)	1.4	0.02
GWSS25	Kandam	0.55	0.02
GWSS26	Hamma-Ali	0.4	0.02
GWSS55	Kebbe	0.23	0.02

Abbreviation and Symbol definition: Distance from contaminants source.

High concentration of Cd in waters may be attributed to anthropogenic inputs from sources such as auto repairs workshops, woodworks, tanneries, limestone mining, local aluminum utensil production, gold mining, and the Nigeria cement factory activities in the study area.

vii. Chromium (Cr): Chromium is an essential micronutrient for animals and plants. It is an essential nutrient in man because it helps the body in the utilization of sugar, protein and fats but only at low concentrations. In groundwater, it may be present both from anthropogenic or natural sources. In this study the mean concentration of Cr (0.27mg/L) is above WHO (2004) and SON (2007) standards of 0.05mg/L for drinking water. The Cr concentration encountered in the waters of the area is similar to those observed by Bala *et al.*, (2012). Table 4.21, presents the results of Chromium using different recommended standard methods. 4% of sampled water is enriched in chromium content above acceptable limits of WHO (2004) and NIS(2007) for domestic water quality. Chromium contaminant source in the area according to Francis (2005) and Bagudo *et al.*, (2009) may be associated to local chromium plating and alloying activities in the local aluminum utensils production workshops, the metallic wastes that may result in the accumulation of aluminum and alloying metals such as Mn, Ca, Zn, Cr, Cd, Fe, ...Pb. This view was also supported by the studies of Dayan and Paine (2001) and Dabonne *et al.*, (2010). Cement, tanning and paint processing could also be contributing to sources of chromium in the area. It is also present in minerals (dunites and serpentinites).

Table 4.21 Assessment of Cr (mg/L) in waters of Sokoto Basin Using Various standards

Station ID	Location	Distance(km)	Cr(mg/L)	WHO(0.05mg/L)	SON(0.05mg/L)
SRIS42	Rima River		0.8	*	*
SRIS46	Argungu-K...		0.86	*	*
SRI66	Balkori Bridge		0.14	*	*
SRIS27	Rima River		0.22	*	*
SRIS28	Sokoto River		0.22	*	*
SRES15	Rima river		0.24	*	*
GWSS49	Kuka Mairafu	0.2	0.76	*	*
GWSS50	Gidan Gado	0.7	0.91	*	*
GWSS9	Gundumi	0.3	0.16	*	*
GWSS87	YarGeda	0.2	0.12	*	*
GWSS86	Bimasa	0.4	0.26	*	*
GWSS10	Gidan sale	0.2	0.03	*	*
GWSS11	Shinkafi 1	0.1	0.05	√	*
GWSS12	Shinkafi 2	0.15	0.14	*	*
GWSS13	Isa	0.2	0.07	*	*
GWSS14	Tarshar B	0.1	0.15	*	*
GWSS16	Sabon Birnin	0.6	0.28	*	*
GWSS38	Karama D.C	1.2	0.77	*	*
GWSS64	Silame	0.3	0.07	*	*
GWSS78	Ganbuwa	2.2	0.12	*	*
GWSS3	Gidan Madi	0.5	0.04	√	√
GWSS5	Balle	0.2	0.04	√	√
GWSS31	Rundi	1.5	0.63	*	*
GWSS34	Yabo	0.3	0.71	*	*
GWSS35	Shagari	0.4	0.78	*	*
GWSS36	Gwandu	0.2	0.75	*	*
GWSS37	Tambuwal	0.5	0.77	*	*
GWSS39	Kalgo	2.2	0.79	*	*
GWSS40	Birnin Kebbi	1.2	0.66	*	*
GWSS41	Goru	1.0	0.84	*	*
GWSS44	Alwasa	2.3	0.77	*	*
GWSS43	Dageri	0.3	0.87	*	*
GWSS45	Tungan Isiaka	0.2	0.81	*	*
GWSS17	Tsamaye	0.2	0.22	*	*
GWSS21	Marmona	0.6	0.31	*	*
GWSS29	Wammakko	0.1	0.6	*	*
GWSS30	Kalambaina	0.3	0.6	*	*
GWSS32	Bodinga	1.4	0.6	*	*
GWSS33	Lambar Marzuru	0.5	0.69	*	*
GWSS47	Sokoto Town	0.1	0.86	*	*
GWSS48	Sabongari- skt	0.1	0.86	*	*
GWSS51	Sifawa	1.6	0.07	*	*
GWSS52	Jabo	1.0	0.07	*	*
GWSS53	Dogongaji	0.2	0.08	*	*
GWSS54	Barkeji	0.4	0.14	*	*
GWSS65	Tulluwa	0.4	0.14	*	*
GWSS67	Gigane	2.2	0.09	*	*
GWSS68	Illela	0.7	0.15	*	*
GWSS69	Gidan Ciwake	0.4	0.17	*	*
GWSS70	Wauru	0.1	0.13	*	*
GWSS71	Rafin Duma	2.2	0.16	*	*
GWSS73	Rugar Kijo	0.3	0.17	*	*
GWSS75	Salah	0.2	0.2	*	*
GWSS8	Tumbulla	0.56	0.17	*	*
GWSS19	Taloka	0.6	0.25	*	*
GWSS20	Goronyo Town	0.15	0.27	*	*
GWSS1	Kware	1.8	0.3	*	*
GWSS72	Gada	6	0.26	*	*
GWSS22	Wurno	1.6	0.16	*	*
GWSS23	Wurno (Kofar)	1.4	0.16	*	*
GWSS24	Wurno(Kanwuru)	1.4	0.17	*	*
GWSS25	Kandam	0.55	0.2	*	*
GWSS26	Hamma-Ali	0.4	0.2	*	*
GWSS55	Kebbe	0.23	0.12	*	*
GWSS56	Romom Sarki	0.5	0.04	√	√

Abbreviation and Symbol definition: *= above permissible limit; √= within permissible limit, Distance from contamination source.

The presence of chromium in rocks is not common in the study area, and so, the source of Cr is mainly through anthropogenic inputs.

viii. Lead (Pb): Lead is not essential for the growth of human beings. Therefore, the intake of lead should be kept to minimum. Among developing countries, major sources of childhood lead poisoning include lead mining and smelting, paints, leaded gasoline, battery recycling and traditional medicines (Falk, 2003; Meyer *et al.*, 2008). Lead in high doses acts as a metabolic poison causing anemia, chronic neurological disorders in fetuses and children, and behavioral and mental diseases, (Burns and Baghurst, 1999) (Egborge, 1991 and Townsend, 2002). In this study, about 73.5% of sampled waters have lead concentrations above WHO (2004) permissible limits (Table 4.22).

This is not surprising because lead pollution in the area has been reported widely by previous researchers: like Abdu and Yusuf (2013) who reported high concentrations of Pb in both soil and plants in the Zamfara environment. Also, Yi *et al.*, (2012) investigated the extent of childhood lead poisoning and lead contamination among villages in Zamfara State; Bala *et al.*, (2012a) discovered high lead contents in the liver of cattle aged group 0-2 years in Sokoto Abattoir; Ekwumemgbo *et al.*, (2014) evaluated distribution of cadmium (Cd) and lead (Pb) in six geochemical extractable fractions in soil samples obtained from Lambar-gudu mining site in Daretta village, Zamfara State, Nigeria. The determination of the levels of heavy metals in the cement samples in Sokoto for its potential harmfulness on humans and the environment was assessed by Ibrahim *et al.*, 2012; Shabanda *et al.*, (2012) and Yahaya, (2010).

Table 4.22 Assessment of Pb (mg/L) in waters of Sokoto Basin Using Various permissible limits

Station ID	Location	Dist(km)	Pb(mg/L)	WHO(0.01mg/L)	NIS(0.01mg/L)
SRIS15	Rima river		0.26	*	√
SRIS42	Rima River		0.02	*	√
SRIS46	Argungu-K...		0.04	*	√
SRI66	Balkori (Shella) R		0.07	*	√
SRES18	Goronyo Dam		0.14	*	√
SRIS27	Rima River		0.22	*	√
SRIS28	Sokoto River		0.12	*	√
GWSS50	Gidan Gado	0.7	0.04	*	√
GWSS9	Gundumi	0.3	0.23	*	√
GWSS10	Gidan sale	0.2	0.23	*	√
GWSS11	Shinkafi 1	0.1	0.25	*	√
GWSS12	Shinkafi 2	0.15	0.24	*	√
GWSS13	Isa	0.2	0.23	*	√
GWSS14	Tarshar B	0.1	0.24	*	√
GWSS16	Sabon Birnin	0.6	0.21	*	√
GWSS38	Karama D.C	1.2	0.02	*	√
GWSS64	Silame	0.3	0.11	*	√
GWSS78	Ganbuwa	2.2	0.09	*	√
GWSS2	Binji	0.6	0.34	*	√
GWSS3	Gidan Madi	0.5	0.26	*	√
GWSS4	Tangaza	0.4	0.22	*	√
GWSS5	Balle	0.2	0.23	*	√
GWSS31	Rundi	1.5	0.02	*	√
GWSS34	Yabo	0.3	0.03	*	√
GWSS35	Shagari	0.4	0.04	*	√
GWSS36	Gwandu	0.2	0.02	*	√
GWSS37	Tambuwal	0.5	0.03	*	√
GWSS39	Kalgo	2.2	0.02	*	√
GWSS41	Goru	1.0	0.06	*	√
GWSS43	Dageri	0.3	0.03	*	√
GWSS45	Tungan Isiaka	0.2	0.02	*	√
GWSS6	Gwadabawa	0.1	0.2	*	√
GWSS7	Mammasuka	0.12	0.25	*	√
GWSS17	Tsamaye	0.2	0.22	*	√
GWSS21	Marmona	0.6	0.2	*	√
GWSS29	Wammakko	0.1	0.2	*	√
GWSS30	Kalambaina	0.3	0.14	*	√
GWSS32	Bodinga	1.4	0.04	*	√
GWSS33	Lambar Marzuru	0.5	0.04	*	√
GWSS48	Sabongari-S	0.1	0.05	*	√
GWSS51	Sifawa	1.6	0.28	*	√
GWSS53	Dogongaji	0.2	0.09	*	√
GWSS54	Barkeji	2.2	0.02	*	√
GWSS65	Tulluwa	0.4	0.04	*	√
GWSS67	Gigane	2.2	0.04	*	√
GWSS68	Illela	0.7	0.09	*	√
GWSS69	Gidan Ciwake	0.4	0.14	*	√
GWSS70	Wauru	0.1	0.13	*	√
GWSS71	Rafin Duma	2.2	0.14	*	√
GWSS73	Rugar Kijo	0.3	0.13	*	√
GWSS75	Salah	0.2	0.09	*	√
GWSS8	Tumbulla	0.56	0.22	*	√
GWSS20	Goronyo Town	0.15	0.21	*	√
GWSS1	Kware	1.8	0.43	*	√
GWSS74	Bancho	2.4	0.14	*	√
GWSS72	Gada	6	0.12	*	√
GWSS22	Wurno	1.6	0.16	*	√
GWSS23	Wurno (Kofar)	1.4	0.17	*	√
GWSS24	Wurno(Kanu)	1.4	0.2	*	√
GWSS25	Kandam	0.5	0.2	*	√
GWSS26	Hamma-Ali	0.4	0.22	*	√
GWSS55	Kebbe	0.23	0.23	*	√
GWSS56	Romom Sarki	0.5	0.2	*	√

Symbol definition: *= above permissible limit; √= within permissible limit

From the previous studies fore mentioned, the source of lead measured in the area may not only be attributed to wastes generated from anthropogenic sources in the area (Cement Factory, Abattoir, gold mining,... limestone mining); but also to local aluminum utensils manufacturing (that usually take place in the market), the disposal of the by-products into the river could also contribute to lead dispersion in the area, the flow of rivers across the states could also transport lead to uncontaminated sites. Also leachates from dumpsites, combustion of leaded gasoline, spent gasoline from road side automobile mechanic workshops located near surface water bodies especially along Ilela road and surface water sampled at Argungu Kangiwa road, probably have contributed to lead distribution in the area, (Table 4.22).

Generally, the source of the high lead concentration measured in the study area can be associated to different sources (see Table 4.23).

Table 4.23 Distance of few identified contaminant source from the study area.

Contaminant source	Distance(km)	Surface water
Cement Factory	0.6	Sokoto river
Abattoir	1.0	Sokoto river
Air port	4.0	Sokoto river
Hospital	2.2	Sokoto river
Market	0.6	Sokoto river
Tannery	0.3	Rima river
Dumpsite...	0.1	Sokoto and Rima river

The contamination index should be evaluated before an effective conclusion on degree of contamination/ pollution can be made.

4.6.2 Evaluation of Degree of Contamination (CD) for Heavy Metals

Contamination index (CI) summarizes the combined effects of several quality parameters considered harmful to domestic water (Backman *et al.* 1997). The degree of contamination (CD) was used in this case as a measure for contamination index (CI). CD was calculated for every sample independently, values were grouped into three categories regarding contamination level as follows: low contamination is reported if CD values are lower than one ($CD < 1$), medium contamination when CD is between 1 and 3, and when CD is greater than three ($CD > 3$) contamination is high (Aktar *et al.*, 2010, Onkar and Sulochana, 2015).

Another index used to determine degree of contamination is the heavy metal evaluation index (HEI or MI) (Ameh and Akpah, 2011, Onkar and Sulochana 2015), which gives an overall quality of the water with respect to heavy metals (Edet and Offiong, 2002). The higher the concentration of a metal compared to its respective MAC value the worse the quality of water. MI value > 1 is a threshold of warning, (Ameh and Akpah, 2011). These indices are able to predict pollution trends for the future, (Ionescu *et al.*, 2015). Calculated values of Degree of Contamination and the corresponding Metal Index of the heavy metals analyzed are presented in Table 4.24, Appendix XV.

Table 4.24 Heavy Metals Evaluated Indices (Degree of Contamination, CD and Metal index MI) of waters in the Sokoto Basin.

Station ID	Location	Sample ID	CD(WHO)	MI(WHO)	CD(SON)	MI(SON)
GWSS49	Kuka Mairafu	BA	13.33	16.33	12.39	15.39
GWSS50	Gidan Gado	BA	18.76	21.76	15.55	18.55
GWSS9	Gundumi	GU	23.28	26.28	0.76	3.76
GWSS87	YarGeda	GU	-0.14	2.86	0.66	3.66
GWSS86	Bimasa	GU	3.05	6.05	4.58	7.58
GWSS10	Gidan sale	GU-02	20.76	23.76	-1.76	1.24
GWSS11	Shinkafi 1	GU-03	22.88	25.88	-1.40	1.60
GWSS12	Shinkafi 2	GU-04	23.26	26.26	0.35	3.35
GWSS13	Isa	GU-05	21.38	24.38	-0.95	2.05
GWSS14	Tarshar Bagaruwa	GU-06	24.31	27.31	2.57	5.57
SRES15	Rima river	GU-07	28.16	31.16	2.52	5.52
GWSS16	Sabon Birnin	GU-08	23.86	26.86	3.19	6.19
GWSS38	Karama Damba Community	GU-09	14.12	17.12	12.46	15.46
GWSS64	Silame	GW	10.15	13.15	0.60	3.60
GWSS78	Ganbuwa	GW	8.83	11.83	1.82	4.82
GWSS2	Binji	GW-01	31.23	34.23	-2.05	0.96
GWSS3	Gidan Madi	GW-02	23.65	26.65	-1.44	1.57
GWSS4	Tangaza	GW-03	18.50	21.50	-2.46	0.54
GWSS5	Balle	GW-04	20.60	23.60	-1.63	1.37
GWSS31	Rundi	GW-05	11.60	14.60	9.65	12.65
GWSS34	Yabo	GW-06	13.68	16.68	11.24	14.24
GWSS35	Shagari (Government day Secondary Schoo)	GW-08	16.67	19.67	12.90	15.90
GWSS36	Gwandu	GW-09	13.66	16.66	12.40	15.40
GWSS37	Tambuwal	GW-10	15.45	18.45	12.60	15.60
GWSS39	Kalgo Police Barrack	GW-11	14.63	17.63	12.95	15.95
GWSS40	Birnin Kebbi	GW-12	10.47	13.47	10.35	13.35
GWSS41	Goru	GW-13	19.65	22.65	14.13	17.13
SRIS42	Rima River (Birnin Kebbi)	GW-14	15.37	18.37	13.20	16.20
GWSS44	Alwasa	GW-15	13.31	16.31	12.66	15.66
GWSS43	Dageri Primary School	GW-16	17.48	20.48	14.76	17.76
GWSS45	Tungan Isiaka	GW-17	15.70	18.70	13.56	16.56
SRIS46	Argungu-Kangiwa Road	GW-18	18.04	21.04	14.34	17.34
GWSS57	Tambuwal	GW-19	-3.00	0.00	-3.00	0.00
GWSS58	Sanyinna	GW-20	-3.00	0.00	-3.00	0.00
GWSS59	Tiggi	GW-21	-2.99	0.01	-3.00	0.00
GWSS60	Argungu	GW-22	-3.00	0.00	-3.00	0.00
GWSS61	Birnin Kebbi	GW-23	-2.99	0.01	-3.00	0.00
GWSS 62	Kalgo	GW-24	-2.99	0.01	-2.99	0.01
GWSS63	katami	GW-26	-2.99	0.01	-3.00	0.00
GWSS75	Salah	GW-28	-2.99	0.01	-2.99	0.01
GWSS76	Gundun	GW-29	-2.98	0.02	-2.99	0.01
GWSS81	Shuni	KA	-3.00	0.00	-2.99	0.01
GWSS82	Rabah	kA	-3.00	0.00	-2.99	0.01
GWSS83	Chacho	KA	-3.00	0.00	-2.99	0.01
GWSS84	Sokoto Town	KA	-2.99	0.01	-2.99	0.01

Table 4.24 Extn Heavy metals evaluation Indices (Degree of Contamination, CD and Metal index MI) of waters in the Sokoto basin.

Station ID	Location	Sample ID	CD(WHO)	MI(WHO)	CD(SON)	MI(SON)
GWSS85	Sokoto Town (Sama Road.Pumping Station)	KA	-2.99	0.01	-2.99	0.01
SRES80	Shagari Dam	KA-	-2.99	0.01	-3.00	0.00
GWSS6	Gwadabawa	KA-01	17.00	20.00	-2.50	0.50
GWSS7	Mammasuka	KA-02	21.80	24.80	-2.38	0.62
GWSS17	Tsamaye	KA-03	30.53	33.53	23.95	26.95
GWSS21	Marnona	KA-04	22.99	25.99	3.82	6.82
GWSS29	Wammakko	KA-05	29.46	32.46	9.57	12.57
GWSS30	Kalambaina Pri.Sch Hand Pump(HP) Borehole (BH)	KA-06	23.41	26.41	9.44	12.44
GWSS32	Bodinga	KA-07	13.26	16.26	9.17	12.17
GWSS33	Lambar Marzuru	KA-08	14.96	17.96	10.87	13.87
GWSS47	Sokoto Town (FGC)	KA-09	15.27	18.27	14.27	17.27
GWSS48	Sabongari-Sokoto	KA-10	19.51	22.51	14.41	17.41
GWSS51	Sifawa	KA-11	26.49	29.49	0.75	3.75
GWSS52	Jabo	KA-12	-1.29	1.71	-0.62	2.38
GWSS53	Dogongaji	KA-13	8.01	11.01	-0.04	2.97
GWSS54	Barkeji	KA-14	1.67	4.67	0.88	3.88
GWSS65	Tulluwa	KA-15	4.63	7.63	1.71	4.71
SRI66	Balkori Bridge	KA-16	7.45	10.45	2.35	5.35
GWSS67	Gigane	KA-17	3.78	6.78	0.79	3.79
GWSS68	Illela	KA-18	9.37	12.37	2.12	5.12
GWSS69	Gidan Ciwake	KA-19	15.03	18.03	2.81	5.81
GWSS70	Wauru	KA-20	13.09	16.09	2.77	5.77
GWSS71	Rafin Duma	KA-21	15.13	18.13	2.36	5.36
GWSS73	Rugar Kijo	KA-23	14.05	17.05	2.65	5.65
GWSS75	Salah	KA-25	10.67	13.67	3.17	6.17
GWSS 62	Kalgo	KA-25	6.84	9.84	2.29	5.29
GWSS8	Tumbulla	TA-01	19.18	22.18	-2.37	0.63
SRES18	Goronyo Dam	TA-02	2.04	5.04	2.04	5.04
GWSS19	Taloka	TA-03	10.03	13.03	25.16	28.16
GWSS20	Goronyo Town	TA-04	24.04	27.04	3.47	6.47
GWSS1	Kware	W-01	40.53	43.53	-1.22	1.78
GWSS74	Bancho	WU	11.93	14.93	-0.74	2.26
GWSS79	Yabo (Torankawa)	WU	2.77	5.77	4.10	7.10
GWSS72	Gada	WU	12.49	15.49	2.45	5.45
GWSS22	Wurno	WU-02	17.19	20.19	2.57	5.57
GWSS23	Wurno (Kofar Rima)	WU-03	18.15	21.15	2.75	5.75
GWSS24	Wurno(Kanwuru)	WU-04	21.51	24.51	3.38	6.38
GWSS25	Kandam	WU-05	21.87	24.87	3.45	6.45
GWSS26	Hamma-Ali	WU-06	24.10	27.10	4.05	7.05
SRIS27	Rima River(Illa Sokoto Road)	WU-07	23.81	26.81	4.18	7.18
SRIS28	Sokoto River	WU-08	12.13	15.13	1.90	4.90
GWSS55	Kebbe	WU-09	20.60	23.60	-1.63	1.37
GWSS56	Romom Sarki	WU-10	17.00	15.99	-2.50	0.50
Min			-3.00	0.00	-3.00	0.00
Max			40.53	43.53	25.16	28.16
Mean			12.99	15.95	3.76	6.76

CD= Degree of Contamination; MetalIndex; MI; HEI= Heavy metal index

The heavy metal contamination index of selected heavy metals was calculated individually using the standards presented in Table 4.17. The metals considered include Cd, Cr, Fe and Pb. The evaluation indices were computed with maximum permissible standard limits of WHO (2004) and SON (2007) respectively, (Table 4.24). The degree of contamination, CD was used as a reference to estimate the extent of metal pollution (Al-Ami *et al.*, 1987). The range and mean values of CD calculated in this study (using standard specifications of WHO (2004), and SON (2007) were -3.00-40.53; (mean=12.99); and -3.00-25.16 (mean=3.76) respectively. The mean value of contamination index exceed 3 in WHO (2004), and SON (2007) limits, suggesting that the waters are contaminated. The extreme and mean values of HEI, also using WHO (2004) and SON (2007) specified standard were 0.00-43.53 (mean=15.95) and 0.00-28.16 (mean=6.76) respectively. By following the approach of Edet and Offiong (2002), the proposed MI criteria for the samples are as follows: low (MI=10), medium (MI = 10-20) and high (MI =20). The present level of MI considering MI(WHO, 2004) and MI(SON, 2007) shows that the water quality falls within medium to low zone of contamination. Closely related results was observed in previous studies in different locations.

The same observations are found in inland waters of Hong Kong (Zhou *et al.*, 1998). Khan *et al.*, (2005) also, stated that some elevated concentrations of heavy metals (Pb, Cr, Hg, Cd, Fe, Cu, Ni, Zn) were recorded in the surface water bodies near brewery, textile, cement and tanning industries due to their untreated wastewater discharges; and fly ash ponds and industrial effluents from industrial complex. Elmaci *et al.*, (2007) reported high heavy metal concentrations in waters sampled due to the industrial and domestic discharges. Glenn *et al.*, (2009) noted that presence of heavy metals in the coastal lagoon of Manila bay were due to the direct deposition of these metals from polluted air. Panday *et al.*, (2010) observed that in Ganga river, more than 80% of the water samples had Cadmium and Nickel levels above the

recommended maximum permissible concentrations. Bala *et al.*, (2012) reported 100% positive chromium in all samples of liver and kidney of cattle from Sokoto abattoir Nigeria. Likewise, Ibrahim *et al.*, (2012) reported concentration levels of heavy metals in the cement samples from Sokoto to be above the acceptable limit. Abdu and Yusuf (2013) recorded concentration of lead in all samples of soil and water from farmland, in Zamfara State far higher than the acceptable levels. Similar observations were made in soil samples of selected locations in Zamfara state by Ekwumengboet *al.*,(2014).

Similar observations were also made in the present study where concentrations of Pb, Cr and Cd are above the maximum permissible concentrations recommended by WHO (2004) and SON(2007) in most locations. Thus from the degree of contamination assessed, the waters were contaminated and this was confirmed by evaluating the heavy metal indices which revealed that the contamination state varied between low and medium. This suggests that the basin is prone to heavy metal pollution in the near future and this will pose a big threat to living organism (Man. Aquatic life, flora, fauna) existing there.

If this trend is allowed to continue unabated, the environment will be prone to high risk of heavy metal contamination. Hence, strict management actions should be taken into consideration in order to presently protect the environment and preserve it, in the interest of the future users.

4.7 Water quality Assessment and Evaluation for Different Uses

The studied water samples have been evaluated for use in drinking, domestic activities, industrial activities and agricultural purposes (Aquaculture, Livestock and Irrigation).

4.7.5 Evaluation of waters from the Basin for Drinking

Comparing the results of the chemical analyses of the water samples from this study with WHO and SON standards for drinking water in arid regions (Table 4.25) waters in the study

area are suitable for domestic purpose, considering that the results obtained were within recommended limit for WHO and SON. More so, one sample in Rima Group (Taloka-GWS19) is adjudged to be of good to moderate quality due to the excess in its sulphate (8.93 meq/L). However, in construction industry, sulphate content of water is important to avoid deterioration of concrete. To take care of such problems, sulphate resisting cements are developed to suit a range of sulphate concentrations in the soil and water (Lloyd and Heathcote, 1985). As such, such water will be economically wise to be utilized in construction industries.

Table 4.25 Physico-chemical constituents of investigated waters assessed with Standards for drinking water by (SON, 2007 and WHO, 2004).

Parameters	Measured Range	WHO	SON
TDS (mg/L)	0.00-1280	0-1000	0-1500
Na (meq/L)	0.036-30.43	0-8.6	-
Mg (meq/L)	0.032-0.72	-	0-12.34
Cl (meq/L)	0.318-4.926	0-7.04	0-2.5
SO ₄ (meq/L)	0.035-1.083	0-8.3	0-5.2

In this study, the waters of the Basin are within acceptable standard for drinking purpose (WHO, 2004 and SON, 2007). However, 2.2% of samples had TDS concentration above (WHO, 2004) permissible limit for drinking water and this due to contaminate from geogenic and anthropogenic input.

4.7.6 Assessment of Water Chemical Quality for Domestic Use

Domestic use of water includes laundry and household cleaning. A water quality parameter that determines the suitability of that water for such application is hardness. Hardness which is commonly described as ability of soap to lather easily with water according to Todd (1980)

results from the presence of divalent metallic cations, of calcium and magnesium in groundwater. Hard waters are unsuitable for domestic clean-up exercises. In the present study, carbonate hardness (mg/L) was classified following Durfer and Becker (1964) guideline as shown in Table 4.26.

Table 4.26: Present study hardness quality assessed with hardness guideline by Durfer and Becker (1964).

Present study	Range of hardness	Water description	Evaluation	for
Hardness (%)	(mg/L)		domestic use	
50	0-60	Soft	Excellent	
26.1	61-120	Moderately hard	Permissible	
12.5	121-180	Hard	Unsuitable	
11.36	>180	Very hard	Poor	

The percentage distribution of the hardness data obtained (Table 4.26) shows that 50% of samples are soft, 26.1% are moderately hard, 12.5% are hard and 11.36% are very hard. Grading by Durfer and Becker (1964) classification, most waters of Basin are excellent for domestic use. However, Studies in USA, Canada and Japan indicated that incidence of cardiovascular diseases is more in areas where drinking water is extremely soft (Hem 1989), thus the 50% soft waters recorded are of concern. Besides, water samples from Gigane, Taloka and Wurono Kadam were noted to be hard when compare with BIS (>300mg/L) but were within permissible limit for SON and WHO (500mg/L).

4.7.3 Evaluation of Water Quality for Industrial Use

The quality criteria of water for industrial purposes depend on the type of industry, processes and products. The quality criteria of water for use in boilers are TDS, hardness and no acid reaction. In production of Low pressure boilers, water with total dissolved solids up to 5000

mg/L and CaCO_3 hardness up to 80 mg/L is required, while in high pressure boiler, total dissolved solids should be less than 50 mg/L and CaCO_3 hardness less than 1 mg/L.

In this study, 32% of samples had an acceptable TDS value for high pressure boilers but their respective hardness need to be reduced ($<1.0\text{mg/L}$) to be suitable for use in high pressure boilers while its' not suitable for low pressure boilers ($\text{TDS}<5000\text{mg/L}$). Therefore, water treatment is necessary before use in high pressure boilers production. For the manufacture of pharmaceuticals and high grade paper, water approaching or equaling the quality of distilled water is required (Singhal and Gupta, 2010). Very pure water is also desirable in nuclear reactors to keep the radioactivity caused by neutron activation of dissolved solids as low as possible (Hem 1989).

4.7.4 Evaluation of WaterQuality for Aquaculture

Recently in Nigeria, fish farming has experienced a boom. Water quality determines to a great extent the success or failure of fish cultural operation. In part of the study area at Birnin Kebbi, Argungu International Fishing Festival (Plate III) usually held annually, besides encouraging farmers, it also promotes tourism.



Plate III: Argungu River/fishermen during the Argungu festival, (AzTech, 2010)

Unsuitable water quality habitat may likely promote the growth of water hyacinth upstream and downstream thus affecting growth of fish thereby reducing the size of fish usually harvested in the river, (Plate IV).



Plate IV: The size of fish usually harvested during Argungu International fishing festival, (AzTech, 2010)

Hence, temperature, and pH of water which have direct impact on fish farming were evaluated.

Temperature: Aquatic organisms (like fish) are dependent on certain temperature range for optimal growth. Optimal temperature for fish depend on the species: some survive best in colder water whereas others prefer warm water (EPA, 2003). For Catfish, the temperature range for juveniles is between 32°C and 35°C and for the spawning the acceptable temperature is 29°C, (Beveridge *et al.*, 1994; EPA, 2003). The mean (32.48°C) temperature recorded in the area studied is within acceptable limit for survival of cat fish. This indicates that for the species of fish grown in Nigeria (which are mostly catfish and tilapia), the waters analyzed have tolerable temperatures for aquaculture.

pH: This indicates the hydrogen ion activity, it is commonly known to range between 0-14. The pH values from 0-7 indicate acidity, 7 indicate neutral and 7-14 indicate alkalinity. The pH range for Tilapia fish range between 5-10. The mean pH value measured in the basin is 6.02. It suggests that on the average the waters of the basin are suitable for Tilapia fish rearing. However, there are few outliers where pH value is low (<5.0), suitable alkaline constituent is suggested to be added to neutralize the acidity effect.

4.7.5 Assessment of Groundwater Chemical quality for livestock

Fundamentally, the same standards applicable to human being can be applied for livestock, (Singhal and Gupta, 2010). However, animals can have a greater tolerance of total dissolved solids (1000 mg/L). Standards also depend upon livestock type, age and food habits, (Bouwer 1978; Lloyd and Heathcote 1985), (Plate V).



Plate V: Cattle being used as beasts of burden

Besides salinity requirements, the total dissolved solids are regarded as an overall parameter for the suitability of groundwaters (UNESCO/WHO, 1978) for use by livestock. Most animals tend to use water that is relatively higher in dissolved solids than that which is considered safe for humans. The relevant standards, according to UNESCO/WHO (1978), range from

3000mgTDS/L for poultry up to 10000 mgTDS/L for cattle. But, the classification model of the national Academy of science and National Academy of Engineering (1972) has been used in the present study (Table 4.27).

Table 4.27 Guide for the use of saline waters for livestock and poultry

TDS (mg/L)	Characters
<1000	Relatively low level of salinity. Excellent for all classes of livestock and poultry
1000-2999	Very satisfactory for all classes of livestock and poultry. May cause temporary and mild diarrhea in livestock not accustomed to them or watery droppings in poultry.
3000-4999	Satisfactory for livestock, but may cause temporary diarrhea or be refused at first by animal not accustomed to them. Poor waters for poultry, often causing watery feces, increased mortality and decreased growth, especially in turkey.
5000-6999	Can be used with reasonable safety for dairy and beef cattle, for sheep, swine, and horses. Avoid use for pregnant or lactating animals. Not acceptable for poultry.
7000-10000	Unfit for poultry and probably for swine. Considerable risk in using for pregnant or lactating cows, horses or sheep or for the young of these species. In general, use should be avoided although older ruminants, horses, poultry and swine may subsist on them under certain conditions.
>10000	Risks with these highly saline waters are so great that they cannot be recommended for use under any conditions.

(National Academy of Science and National Academy of Engineering (1972) in Alagbe, 2004).

Considering the model (Table 4.27), except for a few locations, majority of the studied water samples were considered as being excellent for use for all classes of livestock and poultry, Groundwater sample from Sokoto Group Aquifer type (Rafin Duma with TDS of 1280mg/L) and Gigane with TDS of 1040mg/L are few exceptions classified as satisfactory for all classes of livestock and poultry. However, such water may have to be used with caution especially when used for poultry and some other livestock that are not accustomed to such salinity in water, (Alagbe, 2004).

4.7.6 Evaluation of water quality for Irrigation use

Excessive concentrations of dissolved ions in the water used for irrigation affect plants by lowering the osmotic pressure in the plant structural cells. This process prevents water from reaching the branches and leaves, thus reducing the agricultural productivity. The suitability of groundwater for irrigation purpose in this study is discussed based on: TDS, Residual Sodium Carbonate (RSC), Percent Sodium (%Na), Sodium Adsorption Ratio (SAR), and Magnesium Hazard (MH),

i. **TDS:** The TDS is a vital factor for irrigation water due to the impact of specific ions on plant physiology and soil structure (Salah, 1999). Water with high salinity leads to decrease in the efficiency of soil and plant growth. Increase in water salinity increases salts contents in the soil, which leads to salinization problems. The US Environmental Protection Agency (USEPA, 1976) and Wilcox (1955) adopted a classification based on range of TDS for arid and semi-arid regions. It has been found useful in this study. The TDS values of groundwater samples were assessed with USEPA (1976) and Wilcox (1955) classification of TDS for irrigation (Table 4.28).

Table 4.28 TDS classification for irrigation purpose, (USEPA, 1976) and (Wilcox, 1955).

TDS (mg/L)*	Effects on Plants	TDS (mg/L)**	Status
500	No detrimental effects usually noticed	200-1000	Best quality water
500-1000	Detrimental effects on sensitive crops	1000-3000	Water involving hazard
1000-2000	Adverse effects on many crops, requiring careful management practices	3000-7000	Used for irrigation only with leaching and perfect drainage.
2000-5000	Only for tolerant plants on permeable soils with careful management practice		

*= USEPA (1976) classification, **= Wilcox (1955) classification

The waters of the Basin are suitable for irrigation considering the two classification except that in the case of USEPA (1976) grading, GWSS71 and GWSS69 of Sokoto Group Aquifer type with TDS of 1280mg/L and 1040mg/L respectively needs to used with caution perhaps a good agricultural practice and water treatment to yield optimum result when used for farming may be necessary.

ii. Percent Sodium and Residual sodium carbonate Irrigation classification:

One of the earliest system of classification of water for use in irrigation was given by Wilcox (1955) which is based on electrical conductivity (EC), percent sodium (% Na) and boron concentration. When water containing high amounts of Na^+ is applied to soils, sodium tends to displace the Ca^{+2} and Mg^{+2} , then adsorbs to clay minerals and consequently, reduces its permeability. The computed results of percent sodium (%Na), residual sodium carbonate (RSC) and Magnesium Harzard are presented in Table 4. 29 and Appendix XVII.

Table 4.29: RSC, %Na and MH Classification for Irrigation

Station ID	Location	Sample ID	RSC(meq/l)	Grade Code	%Na	Grade Code	MH(meq/l)	Grade code
GWSS49	Kuka Mairafu	BA	1.35	M	31.18	G	28.56	S
GWSS50	Gidan Gado	BA	0.59	S	38.31	G	50.51	U
GWSS9	Gundumi	GU	0.12	S	59.67	P	35.22	S
GWSS87	YarGeda	GU	-0.3	S	37.48	G	29.04	S
GWSS86	Bimasa	GU	-0.02	S	31.37	G	21.95	S
GWSS10	Gidan sale	GU	0.12	S	61.32	D	33.49	S
GWSS11	Shinkafi 1	GU	0.64	S	47.29	P	34	S
GWSS12	Shinkafi 2	GU	1.65	M	68.81	D	41.7	S
GWSS13	Isa	GU	-0.29	S	43.14	P	41.61	S
GWSS14	Tarshar Bagaruwa	GU	4.07	US	94.08	U	26.89	S
SRES15	Rima river	GU	0.17	S	60.75	D	38.57	S
GWSS16	Sabon Birnin	GU	0.08	S	40.23	P	38.38	S
GWSS38	Karama D.Cunity	GU	-0.06	S	47.01	P	27.94	S
GWSS64	Silame	GW	-0.11	S	38.27	G	12.47	S
GWSS78	Ganbuwa	GW	-1.73	S	16.42	E	19.7	S
GWSS2	Binji	GW	0.03	S	46.22	P	37.96	S
GWSS3	Gidan Madi	GW	-0.69	S	65.63	D	32.54	S
GWSS4	Tangaza	GW	0.01	S	41.36	P	39.3	S
GWSS5	Balle	GW	-0.14	S	20.89	G	71.46	U
GWSS31	Rundi	GW	-0.37	S	33.99	G	23.39	S
GWSS34	Yabo	GW	-0.07	S	57.2	P	40.96	S
GWSS35	Shagari (GDSS)	GW	-0.66	S	19.97	E	10.9	S
GWSS36	Gwandu	GW	0.05	S	71.69	D	31.42	S
GWSS37	Tambuwal	GW	0.43	S	31.01	G	13.92	S
GWSS39	Kalgo Police Barrack	GW	0.02	S	75.1	D	38.21	S
GWSS40	Birnin Kebbi	GW	0.16	S	23.02	G	50.7	U
GWSS41	Goru	GW	-0.15	S	56.17	P	37.95	S
SRIS42	Rima River (Birnin Kebbi)	GW	0.2	S	35.93	G	33.47	S
GWSS44	Alwasa	GW	0.04	S	35.29	G	41.86	S
GWSS43	Dageri Primary School	GW	-0.54	S	31.46	G	38.96	S
GWSS45	Tungan Isiaka	GW	1.12	M	49.39	P	55.14	U
SRIS46	Argungu-Kangiwa Road	GW	0.37	S	46.88	P	33.51	S
GWSS57	Tambuwal	GW	-0.21	S	22.4	G	14.38	S
GWSS58	Sanyinna	GW	-0.55	S	15.28	E	24.45	S
GWSS59	Tiggi	GW	-0.15	S	14.56	E	48.8	S
GWSS60	Argungu	GW	-0.33	S	13.07	E	49.05	S
GWSS61	Birnin Kebbi	GW	0.01	S	24.78	G	49.03	S
GWSS 62	Kalgo	GW	-0.3	S	27.1	G	35.12	S
GWSS63	katami	GW	-0.2	S	10.57	E	30.33	S
GWSS75	Salah	GW	-0.73	S	26.9	G	21.91	S
GWSS76	Gundun	GW	-1.53	S	5.34	E	20.12	S

Abbreviation: RSC= Residual Sodium Carbon, E= Excellent, G= Good, P=Permissible D= Doubtful and S= Safe, M=Marginal, U=Unsuitable, BA= Basement Complex, GU= Gundumi-Ilo Formation, SKT= Sokoto Group, RMG= Rima Group, GW= Gwandu Formation.

Table 4.29 Extn: RSC, %Na and MH Classification for Irrigation

Station ID	Location	Sample ID	RSC (meq/l)	Grade Code	%Na	Grade Code	MH(meq/l)	Grade Code
GWSS81	Shuni	SK	-1.01	S	9.33	E	17.66	S
GWSS82	Rabah	SK	-0.28	S	55.94	P	11.44	S
GWSS83	Chacho	SK	-1.01	S	12.54	E	15.05	S
GWSS84	Sokoto Town 1	SK	-1.06	S	11.37	E	18.78	S
GWSS85	Sokoto Town 11	SK	-1.56	S	15.68	E	13.18	S
SRES80	Shagari Dam	SK	0.27	S	35.65	G	36.15	S
GWSS6	Gwadabawa	SK	-4.61	S	6.67	E	40.86	S
GWSS7	Mammasuka	SK	-1.36	S	21.43	G	30.45	S
GWSS17	Tsamaye	SK	-0.31	S	56.89	P	29.3	S
GWSS21	Marnona	SK	-0.37	S	24.54	G	20.98	S
GWSS29	Wammakko	SK	-3.37	S	6.38	E	31.96	S
GWSS30	Kalambaina	SK	-1.17	S	27.35	G	12.35	S
GWSS32	Bodinga	SK	-0.74	S	31.6	G	22.22	S
GWSS33	Lambar Marzuru	SK	-0.02	S	55.36	P	50.6	U
GWSS47	Sokoto Town (FGC)	SK	-0.36	S	7.32	E	12.05	S
GWSS48	Sabongari-Sokoto	SK	-0.82	S	15.86	E	18.03	S
GWSS51	Sifawa	SK	-0.08	S	38.93	G	17.49	S
GWSS52	Jabo	SK	-0.25	S	31.21	G	9.2	S
GWSS53	Dogongaji	SK	-0.14	S	11.3	E	9.61	S
GWSS54	Barkeji	SK	0.05	S	10.03	E	17.02	S
GWSS65	Tulluwa	SK	-0.52	S	3.73	E	13.34	S
SRI66	Balkori Bridge	SK	-0.45	S	4.31	E	36.69	S
GWSS67	Gigane	SK	-8.56	S	27.43	G	38.43	S
GWSS68	Illela	SK	-2.39	S	17.83	E	57.58	U
GWSS69	Gidan Ciwake	SK	-6.42	S	37.75	G	38.18	S
GWSS70	Wauru	SK	-5.14	S	44.61	P	37.24	S
GWSS71	Rafin Duma	SK	0.01	S	24.78	G	49.03	S
GWSS73	Rugar Kijo	SK	0	S	19.05	E	12.67	S
GWSS75	Salah	SK	-0.33	S	3.57	E	33.1	S
GWSS8	Tumbulla	RM	0.11	S	56.69	P	10.04	S
SRES18	Goronyo Dam	RM	0.27	S	54.52	P	36.88	S
GWSS19	Taloka	RM	-2.96	S	51.37	P	42.49	S
GWSS20	Goronyo Town	RM	0.52	S	53.45	P	29.92	S
GWSS1	Kware	RM	-0.62	S	7.39	E	10.25	S
GWSS74	Bancho	RM	-0.11	S	38.27	G	12.47	S
GWSS79	Yabo (Torankawa)	RM	-0.21	S	49.86	P	41.23	S
GWSS72	Gada	RM	-6.02	S	13.62	E	24.64	S
GWSS22	Wurno	RM	-1.35	S	18.43	E	24.22	S
GWSS23	Wurno (Kofar Rima)	RM	-0.93	S	27.23	G	30.69	S
GWSS24	Wurno(Kanwuru)	RM	-7.53	S	14.47	E	28.96	S
GWSS25	Kandam	RM	-0.69	S	19.14	E	30.37	S
GWSS26	Hamma-Ali	RM	-1.56	S	19.51	E	30.48	S
SRIS27	Rima River	RM	0.18	S	35.91	G	31.76	S
SRIS28	Sokoto River	RM	0.16	S	37.46	G	32.62	S
GWSS55	Kebbe	RM	-2.92	S	25.71	G	30.72	S
GWSS56	Romom Sarki	RM	-0.1	S	15.99	E	14.88	S

Abbreviation: RSC= Residual Sodium Carbon, E= Excellent, G= Good, P=Permissible D= Doubtful and S= Safe, M=Marginal, U=Unsuitable, BA= Basement Complex, GU= Gundumi-Ilo Formation, SKT= Sokoto Group, RMG= Rima Group, GW= Gwandu Formation.

In this study, according to Wilcox (1948) %Na classification of water for irrigation purpose, (Table 4.29), 22.9% of the waters are dominantly permissible for irrigation, 34.83% are good for irrigation use, 33.33% are ‘excellent’ for the purpose of irrigation, 6.89% are doubtful and 1.14% are unsuitable for irrigation.

The percent sodium computed was evaluated using the irrigation water quality classification, Table (4.30) (Wilcox, 1948)

Table 4.30 Percent Sodium Irrigation classification, (Wilcox, 1948).

Water Class	%Na	Cond	Salinity Hazard
Excellent (E)	<20	250	Low
Good (G)	20-40	250-750	Medium
Permissible (P)	40-60	750-2000	High
Doubtful (D)	60-80	2000-3000	Very High
Unsuitable (U)	>80	>3000	Very High

Generally, the basin waters are suitable for irrigation except in few locations where the waters are classified: permissible and doubtful, upgrading of other factors that promote irrigation practice is advise and the Unsuitable at Tarsha Bagaru cannot be used for irrigation base on (Wilcox, 1948) percent sodium classification of water for irrigation purpose.

iii Residual Sodium Carbon (RSC)

RSC is another technique by which water parameters can be assessed for irrigation use. It is used to distinguish between the different classes of water for irrigation purpose. The water, which contains high amounts of bicarbonate and relatively low in Calcium and Magnesium, is considered hazardous water for irrigation. By evaporation of water from soils, Ca^{2+} and Mg^{+2} can precipitate the CO_3^{2-} and HCO_3^- which can affect plant growth. Richard (1954) stated that

waters having RSC less than 1.25meq/L are classified as generally safe for irrigation, those with RSC of 1.25to 2.5 meq/L are marginal waters and those with RSC greater than 2.5meq/L are considered unsuitable waters for irrigation purposes.RSC value considers the bicarbonate of water. Ahigh concentration of bicarbonate leads to increase in the pH value of water that causes dissolution of organic matter and also lead to precipitation of calcium and magnesium that can cause an increase in sodium content in the soil.

According to Richard (1954) classification, generally in the study, 1% of the water samples are unsuitable for irrigation purpose, 4% are graded as marginal indicating that water can be used for irrigation but under certain conditions and 95% are safe for irrigation use.

iv Assessment of water for irrigation purpose applying Salinity Hazard method:

The US Salinity Laboratory of the US Department of Agriculture used salinity hazard and sodium hazard as the two important criteria for the classification of irrigation waters. Salinity hazard is a measure of EC and sodium hazard is expressed in terms of Sodium Adsorption Ratio (SAR).Adjusted SAR has been suggested as other criteria to assess the suitability of water for irrigation (Ayers 1975).High value of SAR implies that sodium in the water may replace calcium and magnesium ions in the soil, potentially causing damage to the soil structure. Table (4.31)summarizes the significance and interpretation of different water quality classes based on the combination of the hazards due to salinity expressed as electrical conductivity in uS/cm and the hazard due to sodium concentration expressed as SAR values after Richard (1954). Figure (4.37) is the water samples evaluation from the studied area using a widely used monogram for evaluation of water for irrigation purpose after, Wilcox, (1955).

Table 4.31 Significance and interpretation of the water quality classes according to Richard(1954)

Cond	Quality	Range	Usage	SAR	Quality	Range	Usage
C1	Low salinity	100-250	Can be used for irrigation with most soil with likelihood that the soil salinity will develop	S1	Low salinity	0-10	Can be used for all soils. Preferably used with good permeability. Can produce a harmful effect, good soil management essential. Unsuitable for irrigation purposes expect at low and perhaps medium salinity
C2	Medium salinity	250-750	Can be used if moderate leaching occurs	S2	Medium salinity	10-18	
C3	High salinity	750-2250	Cannot be used with restricted drainage	S3	High salinity	18-26	
C4	Very high salinity	>2250	Is not suitable for irrigation under ordinary conditions but may be used occasionally under very special circumstances	S4	very high Salinity	26-100	

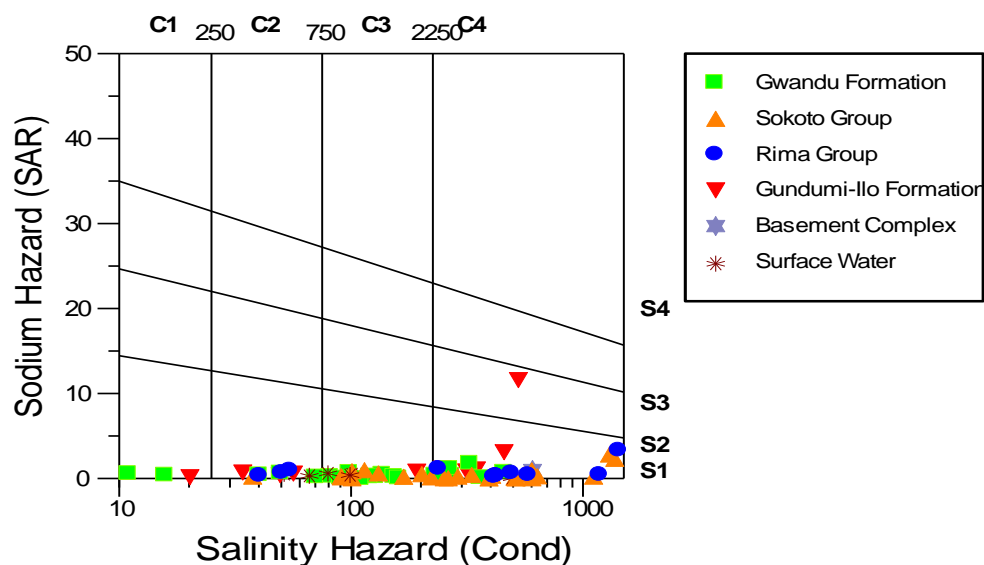


Fig 4.37 Wilcox classification of sampled waters from the study area

The study of the distribution of the groundwater samples from this area within the monogram (Fig 4.37) revealed the following results: 4% of the waters samples fall within the C1-S1 class.

They have low salinity and also low sodium hazards. These waters can be used to irrigate all crops on all types of soils. The class C2-S1 Field is occupied by 16.9% of the water samples. Such waters possess medium salinity and low sodium-ion content. The water samples of this category can be used for irrigation on almost all soils. 32.3% of water samples are identified within the class C3-S1. This group therefore possesses high salinity but low sodium-ion content and can be used for irrigation purpose under special conditions. 45% of water samples were linked to this C4-S1 class suggesting that the waters can be used for irrigation but with extreme caution. Finally, C4-S2 class 1% of water samples were associated to this group indicating that this kind of water is not suitable for irrigation under ordinary conditions but may be used occasionally under very special circumstances, preferably used with good permeability.

v. Magnesium Hazard (MH)

In 1964, a magnesium hazard classification system for assessing the suitability of water quality for irrigation purpose was proposed by Szaboles and Darab, since then it has been widely applied in irrigation assessment studies. It is such that, if MH exceeds 50 meq/L, such water is considered to be harmful and hence is unsuitable for irrigation (Khodapanahet *et al.*, 2009 and Hamza, 2012). In this study, the mean MH recorded is 30.09 meq/L. MH exceeds 50 meq/L in about 6% of the water samples locations (GWSS: 50,5,40,45,33, and 68) and hence are not suitable for irrigation purpose. The remaining 94% have MH less than 50 meq/L and hence suitable for irrigation purpose.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The application of hydro-chemical and environmental isotope approach to study the dynamics of the composition of surface and groundwater resources in the southern part of the Iullemeden (Sokoto) Basin, has been studied and the following conclusions are drawn.

- i. In characterizing the water resources of the Sokoto Basin, three different water types were identified, Ca-HCO₃; Ca-SO₄; and Na-HCO₃. With the aid of the piper diagram the rock types being tapped (Carbonate rock and Evaporite rock) were confirmed based on three hydrochemical facies (AD facie, EG facie and facie) realized. The chemical compositions of the waters from the aquifer system of Sokoto Basin were showed to be controlled by mainly dissolution of aquifer materials. Similarly, the isotope signature ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and T) of the waters show that the waters of the basin are characterized by moderately depleted stable isotope signatures, Paleowaters which are more depleted compared to young waters; and evaporated waters which are most enriched in stable isotope signatures.
- ii. The study was able to establish based on the findings that contrary to earlier claims and beliefs, Continental Intercalaire aquifer receives modern water as recharge and the water compositions of the aquifers are related as such the waters of the aquifers are interrelated.
- iii. The potential water contaminants and determination of suitability of the waters for different uses were also studied. The concentration of physico-chemical constituents in the water samples were compared with prominent standards for water quality, to determine the suitability of water for drinking. The heavy metal indices were calculated to determine the degree of contamination of the waters of the basin. The results showed that, the water quality of the aquifers of the basin are acceptable for drinking as well as for other purposes. The

waters are generally relatively acidic to slightly basic, with pH ranged from 3.21 to 7.53 (mean=5.75). The TDS falls under fresh water to brackish categories. The Total hardness as measured was categorized under soft to very hard. The Fluoride concentrations in the waters were permissible for drinking. However, the fluoride concentrations at Gigane well of Sokoto Group aquifer exceeded the permissible limit for drinking water (6.45mg/L). The mean concentration of chloride, nitrate, boron, iron, lead and cadmium as measured, were within the permissible limits for drinking water although there are few exceptions recorded. The high concentrations observed, were associated with diffuse and point pollutants sources (Abattoir, use of organic and inorganic fertilizers on farm land, indiscriminate siting of human septic tanks, dumpsites and drainage systems (gutters), in close proximity to wells; and disposal of industrial waste into surface water without prior treatment. These contamination sources also contributed to the high mean concentrations of chromium observed (0.27mg/L). The degree of contamination of heavy metals was in the low to medium zones.

iv. Water analyses for Sodium Adsorption Ratio (SAR), percent Sodium (%Na), residual sodium carbonate (RSC) and magnesium hazard revealed that most of the waters of the basin are suitable for irrigation following the quality classification of Wilcox and US salinity classification. However, few waters were rated unsuitable for irrigation this was attributed to influences of urban and industrial activities, weathering and arid climate conditions. This situation can be remediated through application of appropriate treatment strategies.

5.3

Recommendations

i. Strict water resources management actions should be ensured in order to enforce right environmental laws that will protect riparian water bodies.

- ii. The quantity of modern water recharging the aquifer system of the basin and age of the waters should be determined.
- iii. The climate variability and soil assessment for contamination index should be conducted.

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